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PROGRESS REPORT
of the
SOUTHERN UTILIZATION RESEARCH AND
DEVELOPMENT DIVISION
AGRICULTURAL RESEARCH SERVICE

This progress report includes a summary of the current research of the Division and a preliminary report of progress made during the preceding year. It is primarily a tool for use of scientists and administrators in program coordination, development and evaluation; and for use of advisory committees in program review and development of recommendations for future research programs.

The summaries of progress on USDA and cooperative research include some tentative results that have not been tested sufficiently to justify general release. Such findings, when adequately confirmed, will be released promptly through established channels. Because of this, the report is not intended for publication and should not be referred to in literature citations. Copies are distributed only to members of Department staff, advisory committee members and others having a special interest in the development of public agricultural research programs.

This report also includes a list of publications reporting results of USDA and cooperative research issued between July 1, 1967, and June 30, 1968. Current agricultural research findings are also published in the monthly USDA publication, Agricultural Research. This progress report was compiled in the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, New Orleans 70124, Louisiana.

UNITED STATES DEPARTMENT OF AGRICULTURE

Washington, D. C.

July 1, 1968

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COMMUNICATIONS SECTION

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INTRODUCTION

Organization of the Division

The Southern Utilization Research and Development Division currently conducts research on cotton, cottonseed, peanuts, citrus and subtropical fruits, rice, sweet sorghum, naval stores, cucumbers, sweetpotatoes, and other vegetables. The program includes basic and applied research in the physical and biological sciences and engineering. Basic research plays a key role in uncovering new information that later may be exploited in applied research and development. When appropriate, engineers carry out pilot-plant studies of promising laboratory developments to provide engineering and cost data essential to determining feasibility for industrial application. Division scientists consult with specialists from other organizations during both the planning and the execution of the research, and cooperate actively with industry to facilitate commercialization and utilization of new findings.

The Division's research staff is organized into eight commodity-oriented Laboratories (Cotton Finishes, Cotton Chemical Reactions, Cotton Mechanical, Cotton Physical Properties, Oilseed Crops, Food Crops, Fruit and Vegetable Products, and Naval Stores), and one Laboratory (Engineering and Development) for engineering research and development. Two Pioneering Research Laboratories (Plant Fibers and Seed Protein) were disbanded because one of the Chief Research Chemists retired and the other transferred to Washington.

Headquarters of the Division are located at the Southern Regional Research Laboratory, New Orleans, Louisiana. The Division also has personnel and laboratory facilities at Winter Haven and Olustee, Florida; Weslaco, Texas; Raleigh, North Carolina; and Natick, Massachusetts.

Examples of Outstanding Accomplishments

Soil Release Finish Improves Cotton's Position in the Durable-Press Market. An estimated two million bales of cotton are used annually for end uses in which soil resistance and ease of soil removal are of significant importance. Research by USDA scientists has led to the commercial production of wash-wear and durable-press cottons that soil less readily, clean more easily, and stay brighter during their service life. This enhancement of cotton's position in a lucrative market was achieved by the development of a practical soil release finish that simultaneously imparts wash-wear or durable-press properties to cotton. The finish is durable to repeated laundering and drycleaning, and its application does not adversely affect either the color or the tensile strength of the cotton. Within a short time after publication of information about the new soil release finish,

the textile industry and chemical manufacturers announced production of at least twelve soil release agents, most--if not all--of which are similar to the one described by the Department researchers. Since then, commercial interest has continued at a high level.

New Flame-Retardant Finish for Cotton Evaluated by Industry and the Military. Each year in the United States alone, an estimated 5,100 persons die and hundreds of thousands suffer non-fatal burns from ignited clothing, bedding, and upholstered furniture. An efficient new flame-retardant finish for cotton recently developed by Department scientists--the THPOH finish--should help reduce these deaths and injuries. This finish, which has excellent commercial potential, has been successfully applied on a mill scale by industry and is also being evaluated by the military. A major chemical company has produced a THPOH preparation for commercial use. The new finish is suitable for many different types of fabrics but, unlike present treatments, it can be applied to lightweight apparel, including sleepwear, since the fabric retains essentially all of its original strength and softness. Another advantage is that the treated fabric exhibits less yellowing when exposed to chlorine bleach. In addition to having potential for increasing the safety of the 354 million pounds of cotton presently used annually in apparel, household, and industrial fabrics, the new finish may help cotton make inroads into the 423 million pound market now held by synthetics.

Practical Process for Producing Cottonseed Flour Being Evaluated Domestically and Abroad. Throughout the world, there is general agreement that protein from new sources must be introduced into the diet of human beings. USDA researchers have responded to this need by devising a method for preparing edible, high-protein flour from cottonseed. This method, called the Liquid-Cyclone Process, concentrates most of the protein in one fraction and simultaneously transfers most of the gossypol, a deleterious pigment of cottonseed, into the other fraction. The first fraction, a fine flour that is bland in flavor and light in color, produces highly acceptable bakery products when mixed with wheat flour. The other fraction, a coarse meal, can be mixed with a feed product or used as fertilizer. Estimates based on numerous experimental runs indicate that the United States could produce about two million tons of cottonseed flour annually, and the rest of the world could produce another six million tons. Economics of the process are favorable. Whereas most of the domestic cottonseed crop is now restricted to livestock feed, which sells for about four cents per pound, the high protein fraction used for food could sell for about nine cents per pound, only half the cost of soybean concentrate. Another attractive feature is that most of the equipment required is the same as that used in many plants which already process cottonseed. At least two domestic firms are investigating the process, and the Agency for International Development

has contracted for construction of a pilot-plant in India, where ten tons of the flour will be produced from Indian cottonseed and then test marketed.

Brine Draining of Cucumbers Saves Pickle Industry Millions of Dollars a Year.

Brine draining, an innovation developed by Department scientists to prevent cucumber pickles from becoming soft and spoiling, is now credited with saving the industry \$25 million a year. The procedure resulted from fundamental research that identified enzymes originating from mold growth in cucumber flowers as the cause of this breakdown in the cellular structure of the cucumbers. After it was discovered that the enzymes were extracted into the brine, the problem was solved by developing a method to detect which vats were involved and then replacing the brine in them. Since then, the use of brine draining has increased steadily: in 1955, the first year that it was used extensively in the southern states, about 2,000,000 bushels of brined cucumbers were drained; in 1967, the procedure was applied to one-third of the crop--6,750,000 bushels in 21 plants. Moreover, although pickles already rank among the five best-selling canned vegetables, the industry, now valued at \$325 million retail, is continuing to grow rapidly; therefore, the present annual saving of \$25 million can also be expected to increase.

AREA 1 - COTTON UTILIZATION

USDA and Cooperative Program

Location of Intramural Work	Scientist Man-Years F.Y. 1968		
	Research Problem Area		
	407	709	Total
Louisiana (New Orleans)	:	:	:
Chemical Composition, Physical Properties and Structure	20.9	:	20.9
Chemical and Physical Investigations to Improve Products	21.3	:	21.3
Technology--Process and Product Development	52.1	10.9	63.0
Total	94.3	10.9	105.2

Intramural program is supplemented by extramural support representing (a) 10.3 SMY's per year at U. S. institutions other than State Agricultural Experiment Stations^{1/}, and (b) P. L. 480 funds in 8 countries representing 411,468 U. S. dollars equivalent per year.

^{1/} RPA 407 - Chemical Composition, Physical Properties and Structure 1.1;
Chemical and Physical Investigations to Improve Products 3.5;
Technology--Process and Product Development 5.7.

Problems and Objectives

Synthetic or "manmade" fibers have aggressively encroached on cotton's markets, gradually reducing its share of the total U. S. mill consumption of all major fibers to less than half. In addition, U. S. capacity for producing cotton can far outpace consumption; even with acreage restrictions, production has frequently exceeded domestic consumption plus exports. Compounding these problems is the fact that over one-fourth of the crop consists of lower quality cottons that are too difficult and expensive to process into commercially acceptable products; hence, in years of normal crop production, these cottons accumulate in public and private stocks despite their lower price. To help solve these problems, utilization research is directed toward the development of fundamental information and technology required for the production of new and improved cotton products to retain present markets and open new ones for this natural fiber.

Major objectives of the research are to develop:

1. Fundamental knowledge of the composition, structure, and properties of native and modified cottons.
2. New or improved techniques and machinery for mechanical processing of cotton.
3. Chemical and physical modifications and treatments to create new or improved cotton products for various end uses.
4. Flame-retardant cotton products to help protect the consumer and reduce loss of property from fire.

Progress - USDA and Cooperative Program

RPA 407 - NEW AND IMPROVED FEED, TEXTILE, AND INDUSTRIAL PRODUCTS FROM FIELD CROPS

A. Chemical Composition, Physical Properties and Structure

1. Adsorption and Swelling Phenomena in Native and Modified Cottons. The change in surface area caused by treatment of cotton fabrics with selected chemical agents was assessed by application of gas adsorption techniques. The surface area increased 18% in fabric samples treated in 50% aqueous dimethylformamide for two hours at room temperature and rinsed but not dried before surface area measurement. Although the area increased 58% after similar treatment in dimethyl sulfoxide, it increased 56% even when the only treatment of the fabric was boiling in distilled water with no reagent added. The effect of other swelling agents and compounds used in the chemical modification of cotton will be evaluated by further study of changes in surface area and in micropores in the fiber structure of cotton treated with these agents.

It has been demonstrated that alkali centrifuge values (ACV's) permit quantitative comparisons of the swellability in caustic solution of native or treated cottons. The forces of yarn twist and fabric weave externally restrict fiber swelling, whereas chemical modifiers exert an internal restraint. When crosslinkages decrease the mobility of the fiber elements or when the interposed chemical reduces the space available to the expanding cellulose, swelling is restricted. ACV's for durable-press samples were found to range from a 15% increase to an 80% decrease over that of the untreated control. An increased ACV suggests an augmentation of space available to the caustic solution, and a decreased ACV suggests limited penetration by the caustic solution. These conclusions were based on data for durable-press cottons that included samples crosslinked with formaldehyde in aqueous, acetic acid, or vapor media and others crosslinked with commercial agents by the polyset or the wet-fixation method. The swellability of the treated cottons was dependent upon such parameters as crosslinking agent, percent add-on, catalyst, type or modification of process, step in noncontinuous procedures, and curing temperature.

Methods and techniques of measuring swelling of cotton by so-called rapid methods have been perfected in contract research at the Polytechnic Institute of Brooklyn. Experimental findings on degree of swelling obtained by these methods are to be correlated with data to be obtained by X-ray diffraction, polarized infrared spectrophotometric techniques, and calorimetric methods.

A study of the physical chemistry and thermodynamics of solution and vapor phase adsorption on and in the cotton fiber has continued under a P. L. 480 project at the Ahmedabad Textile Industry's Research Association, Ahmedabad, India. Heats of wetting of viscose, cotton, and water-swollen cotton in the uncollapsed state were determined as a function of moisture content. Differential heats of wetting of all of the samples indicate that their surfaces are covered with a monolayer of water. Adsorption of formaldehyde was demonstrated to be of the Langmuir type, with bound formaldehyde uniformly distributed throughout the amorphous regions. Form D formaldehyde-treated cotton was shown to have less surface area available to dye and to nitrogen adsorption than Form W cotton. The latter showed no reduction in surface area over that of the untreated cotton. Internal volume of cotton was shown to vary with electrolyte concentration.

In a P. L. 480 project at the Shri Ram Institute for Industrial Research, Delhi, India, progress has been made on a study of the moisture sorption and desorption by crosslinked cotton over the entire humidity range as related to the state of swelling under which the cellulose is crosslinked. Standard cotton was crosslinked with formaldehyde in treating baths containing 2.5, 7, 14, 16, and 19% water to introduce crosslinks at different degrees of swelling. Vapor phase treatments and pad-dry-cure treatments were also made with formaldehyde. The moisture sorption at relative humidities ranging from 10 to 90% was determined with a McBain sorption balance on samples

containing various amounts of formaldehyde. Iodine adsorption values were also determined. Internal surface areas of the cellulose were calculated from the moisture sorption data.

2. Relationships of the Structural Arrangements Within Cotton Fibers to the Physical and Chemical Properties of Native and Modified Cottons.

Microscopical evaluations of various types of chemically modified cottons, including those prepared by the vapor phase method and by conventional methods, are providing new knowledge about ultrastructure and the mechanisms of the chemical modifications. Examination of thin sections of fibers from fabrics crosslinked with methanol hemiformal in the vapor phase showed little crosslinking and nonuniform treatment. Hydroxyethylated cotton treated similarly exhibited a significant amount of crosslinking. Little crosslinking was observed in cotton treated with dimethyldichlorosilane by the vapor phase method. When polyvinyl alcohol (PVA) was used as the embedding medium for sectioning benzyl, benzhydryl, and trityl celluloses, examination of the sections indicated that these cellulose ethers have compact structures. However, use of methacrylate embedding medium caused the ethers to split apart into various patterns. Cellulose esters prepared by esterification of cotton with acid chlorides in dimethylformamide also exhibited compact structures when sectioned in PVA but various structures when sectioned in methacrylate.

The optically measured convolution angles of ten genetic varieties of cotton have been shown to be a function of fiber maturity. When the angle of fiber convolution and the constant spiral angle of the fibrils, also measured optically, were added, the result correlated well with the X-ray orientation angle. Therefore, the variation in X-ray angular measurements found among different genetic varieties may be explained, at least in part, by fiber maturity. Since the strength of cotton is also affected by fiber maturity, the research may lead to a better understanding of the strength-orientation relationship.

Recent work has led to a better understanding of the separate roles of alkali metal ions, hydroxyl ions, and decrystallizing agents in the mechanism of mercerization of cotton. It appears that sodium or higher alkali metal ions are necessary to catalyze the lattice conversion by hydroxyl ions, but prior decrystallization of native cotton also facilitates the conversion.

Benzyltrimethylammonium hydroxide appears to be the most effective agent known for decrystallizing cotton cellulose I without at the same time causing recrystallization and formation of other cellulose lattices. Cotton yarn decrystallized with this agent proved to be highly reactive chemically. It was readily allylated at room temperature without the occurrence of recrystallization. Although subsequent tensioning of the allylated yarn did not cause recrystallization, it did result in a fourfold increase in breaking strength and a sixfold increase in tenacity over that of the untensioned

allylated yarn. The research findings point to the possibility that cellulose crosslinking also could be used to control the amount of recrystallization that occurs, thus yielding wash-wear fabrics of controlled crystallinity.

Further studies of cotton fibers grown at the Texas Agricultural Experiment Station under controlled environmental conditions have shown that medium and high temperatures with alternating cycles of light generally produce fibers more consistent with field-grown cottons having the more desirable characteristics. Low temperatures of growth produce weaker fibers with greater chemical reactivity.

Fiber properties were also determined for cottons grown in an environment of controlled temperature and continuous illumination. Differences in accessibility, crystallinity, and maturity appear to be related to growth temperature through its effect on rate of development of cell wall. Iodine sorption values indicated high accessibility in very immature fibers, whether immaturity was due to stage of growth or to low temperature; accessibility decreased fairly consistently until the boll opened, whereupon a large decrease occurred. X-ray crystallinity index of mature fibers was positively correlated with temperature during fiber growth. Trends in fiber maturity, as determined by microscopical observation, roughly paralleled percentages of cellulose and sugars in relation to age of boll and growth temperature. However, additional data will be needed to more sharply define these various relationships.

A fundamental study of the nature and origin of reversals in cotton fibers and their relationship to mechanical properties of these fibers is continuing in a P. L. 480 project at the University of Ghent, Belgium. Application of a mathematical theory to strength data showed that probably the number of weak places along the cotton fiber axis is significantly higher than the number of reversals. Genetic inheritance of reversal density appears to be complex and probably of a quantitative nature. Correlations between reversal density and other fiber properties were very low, but different varieties of cotton show similar tendencies, that is, a negative correlation with fiber strength and a positive one with length. Irrigation during growth seemed to have no effect on reversal density. It was found that comparison of strength values at and between reversals must be made in the same region on the same fiber to be valid. Under these conditions, the strength at reversals was 75-80% of the strength between reversals for all strength classes and for all varieties tested. Neither relative humidity nor treatment with 18% sodium hydroxide changed this ratio.

Work has continued under a P. L. 480 project at the Fiber Research Institute, T.N.O., in Holland, to investigate the fundamental mechanisms and bonding forces that could be used to improve the tensile strength and other physical properties of cotton textiles. Cotton fibers and yarns--both stretched and relaxed--were swollen to different degrees in sodium hydroxide and then solvent exchanged to remove all sodium hydroxide and water. These cottons

were then crosslinked with diacid chlorides of various chain lengths in dry dimethylformamide, and the physical properties of the crosslinked and control cottons were compared. Results from these exploratory experiments indicate that the fiber data will be more useful than the yarn data. Study of the crosslinking of cotton in various media should yield fundamental information that will be useful in improving the strength characteristics and other properties of cotton textiles.

Research has been initiated at the Central Laboratory, T.N.O., Delft, Holland, under a P. L. 480 grant to investigate the influence of yarn geometry on the response of the structural elements of chemically treated cotton fibers to stress and deformation. All preliminary work on untreated and scoured yarns of various twist multipliers has been completed, and the investigation of chemically treated counterparts of these materials has begun.

3. Mechanisms of Physical Damage to Cotton By Mechanical, Chemical, Physical or Biological Actions. In contract research at the University of Tennessee, shear friction values determined on randomly oriented cotton fibers (card web) were found to be inversely related to tensile modulus of the fibers and directly related to the X-ray angle of the cotton. This indicates that interactions between fibers in mechanical processing are strongly related to fiber structure or tensile stiffness of the fibers. Shear friction of the fibers changed only slightly as relative humidity was increased from 25% to 65%; above 65%, it increased rapidly. The latter rapid increase may explain the desirability of a high humidity in weaving and a low humidity in opening, carding, and drafting. Shear friction decreased as temperature was increased from room temperature to the melting temperature of the cotton wax, and then increased rapidly after the wax had melted. The known changes in mechanical processing behavior of cotton fibers with changes in temperature and humidity are in general agreement with these research findings.

An investigation of the nature and mechanism of the chemical effects of ultraviolet light on cotton cellulose and related compounds is in progress under a P. L. 480 project at the University of Salford, Lancashire, England. The semiconductivity of carbohydrate systems, particularly cotton cellulose systems, was measured to determine the possible exciton states resulting when light interacts with carbohydrates. Semiconduction was observed in carbohydrates with a band energy gap of about 4 electron volts. For D-glucose, xylose, and cyclooctaamylose, the energy gap ranged from 3.6 to 5.5 electron volts, and the semiconduction process was electronic. For cotton cellulose, cyclohexaamylose, cycloheptaamylose, sucrose, and cellobiose, the semiconduction was ionic, and the activation energy of the process was about 1.2 electron volts. Water exerted a profound influence on the semiconduction process in cotton cellulose and other carbohydrates. Semiconductivity measurements offer potential to elucidate the photo-degradation mechanisms of cotton cellulose, both sensitized and unsensitized, particularly as they relate to energy absorption, transport, and localization in the cellulose molecule.

Researchers at the Cotton Technological Research Laboratory, Bombay, India, have completed research under a P. L. 480 grant to investigate the microbial destruction of cotton fibers and fabrics that occurs in exposure during outdoor uses. The activity of enzymes isolated for cellulolytic microorganisms growing on cotton was tested against cellulose and carboxymethyl cellulose. Of those from Aspergilli, the enzyme from A. terreus was most active. Of 15 Streptomyces that were highly cellulolytic, the enzymes from S. ruber and S. scabies were most active. Activity comparisons showed, however, that A. terreus isolate was 16 times more active than that from S. ruber and 49 times more active than that from S. scabies. Kinetic studies also revealed that the streptomyces have two pH optima, one at pH 5.8 and one at pH 7.3. The bimodal nature of the curve was unique in that the reducing sugar produced at both peaks was approximately the same and the enzyme was active even at pH 8.0. By contrast, the optimum for A. terreus was at pH 5.6. Breakdown products of cellulose, found by chromatographic analysis, were glucose, cellobiose, cellotriose, and traces of higher oligosaccharides.

4. Structural and Compositional Changes Occurring During Chemical and Physical Modification of Cotton Cellulose. Changes in the crystallinity of cellulose had a considerable effect on the entire spectrum in the region of 0.7 - 3.0 microns (near infrared). A series of decrystallized cellulose I samples exhibited a progressive loss of spectral structure as crystallinity decreased. Spectra of benzhydryl cellulose and trityl cellulose showed a resolution of the broad O-H stretching band at 3.0 microns into four distinct bands, three of which have been assigned to O-H stretching of intermolecular and intramolecular hydrogen bonds of cellulose II. Unlike crosslinked cottons, these and several other types of chemically modified cottons and oxidized cottons showed changes in spectra in the far infrared region when compared with unmodified cotton. Also, polarized spectra of cellulose films in this region exhibited pronounced changes in relative intensity of certain bands depending upon the direction of the electric vector relative to the direction of chain orientation. These changes may be associated with hydrogen bonding.

The accessibility of Form V (room temperature) formaldehyde-crosslinked cotton fabrics to selected swelling agents, including several concentrations of sodium hydroxide, ethylenediamine, and benzyltrimethylammonium hydroxide, was investigated by means of X-ray diffraction analysis. The degree of restriction was found to be a function of the effective crosslinks present in the sample and of the particular swelling agent used. For example, in an effectively crosslinked fabric sample (1.76% bound formaldehyde) swollen with 12.7% sodium hydroxide, the effect of the swelling agent was completely inhibited. In contrast, when a less effectively crosslinked sample (0.06% formaldehyde) was treated with the same swelling agent, the content of cellulose I decreased from about 80% to 57%, 7% of cellulose II was formed, and amorphous cellulose increased from about 20% to 36%.

Studies have been carried out on the magnetic spectral properties of typical finishing agents such as ethylenebisformamide and methylol compounds to elucidate their structure and their reactivity. Results all show that these compounds undergo slow interconversions of the various conformational forms; this change increases the complexity of the structure. The effects of temperature and solvent on conformational forms of the compounds were also studied. The role that conformational structure plays in imparting specific properties to cellulose is as yet largely unknown.

Application of wide-line nuclear magnetic resonance (NMR) spectroscopic techniques to several different crosslinked cottons has not indicated structural changes that can be attributed to the crosslinking. It now appears that it will be necessary to impose secondary effects, for example swelling of the cottons, to observe such changes by these techniques. A procedure involving the observation of the proton NMR signal of cotton saturated (swollen) with a solution of sodium deuterioxide in heavy water appears promising for providing information on the accessibility of potential reaction sites in the cellulose. Such information will be extremely useful in the development of modified cottons for specific end uses. Computer programs have been developed for plotting the NMR absorption curves, from which spin-spin relaxation times can be determined directly. Dry cotton had a relaxation time of about 10 microseconds.

Methyl vinyl sulfone was reacted under a wide range of conditions with additional forms of cotton, including chopped fibers, ball-milled cellulose, and cellulose dissolved in an appropriate solvent. Total degree of substitution of the methylsulfonyl ethyl groups was a function of both reaction time and reagent concentration; at any given concentration, degree of substitution passed through a maximum at some reaction time. In the heterogeneous reactions, relative distribution of monosubstituents was only slightly affected by reaction media; however, in the homogeneous system, it was considerably affected, particularly at the 3-O-position. Thin-layer chromatographic techniques revealed the presence of several components in the hydrolyzate from a sample of cotton fabric crosslinked with bis-(hydroxyethyl)sulfone. Research in which high temperature gas-liquid chromatography was used to study the products of the reaction between diacetone glucose and divinyl sulfone suggests that this approach could be applied to analysis of hydrolyzates of crosslinked cottons.

An investigation of the chemical nature of cotton modified with tris(1-aziridinyl)phosphine oxide (APO) showed that although the modified cotton possessed excellent wash-wear properties, the extent of crosslinking was very small. This conclusion was based on evidence obtained both by paper electrophoresis of the degradation products and by sol-gel analysis. The distribution of substituents in aminoethylated cotton was found to be 0.27:0.14:1.0 on the hydroxyl groups at carbon-2, carbon-3, and carbon-6. Paper electrophoresis of hydrolyzed aminoethylated cotton showed that about 50% of the nitrogen was in the form of polymerized ethylenimine. The ratio of 2-O- to 6-O-substituted glucoses in cotton treated with diethylaminoethyl

chloride in sodium hydroxide solution decreased as the concentration of the alkali increased. This result suggests that in the more dilute alkali most of the reaction occurs with the hydroxyl groups on the surface of the cotton.

Measurements by reverse gel permeation chromatography were extended to the study of changes produced in decrystallized cotton cellulose by crosslinking with formaldehyde under the conditions of reaction in Forms D, W, V, and C. Marked differences in accessibility and in molecular weight limit of permeability were found to be produced by the various methods of crosslinking. Specifically, accessibility was increased and limit of permeability decreased by Form D; both of these properties were decreased by Form C and increased by Forms W and V. Larger changes in permeation properties were observed at higher levels of crosslinking. Gel permeation measurements indicated that the accessibility of native cotton cellulose was approximately 55% of that of cotton decrystallized by ball milling. Investigation of an improved method of measuring permeability under equilibrium conditions is in progress in order to assess the validity of deductions about the molecular structure of cotton derived from use of the gel permeation technique.

Research studies of chemical modifications of cotton fabrics involving control of lateral molecular order and crosslink distribution have continued under a P. L. 480 grant at the Shirley Institute, Manchester, England. Pertinent data have been developed, the interpretation of which clarifies the structure of cotton cellulose and explains aspects of its reactivity. Chemical evidence points to elementary structural units in cotton cellulose that are of the same general dimensions as those observed in electron microscopy. Only certain of the hydroxyl groups occupying the three positions in the anhydroglucose unit of cellulose are available on the surfaces of the elementary structural units. While the extent of penetration of the cellulose unit has been known to be a function of reaction conditions, data from this study provide a more quantitative relationship. Data on crosslinked compositions are being obtained for interpretation of sites of crosslink attachment.

A fundamental investigation of the effect of swelling and stretching treatments on the fine structure and mechanical properties of cotton fibers has been completed under a P. L. 480 grant at the Ahmedabad Textile Industry's Research Association (ATIRA), in India. Changes in the crystallite structure of cotton fibers swollen in caustic soda, ethylene diamine, and zinc chloride were characterized by optical methods and were related to changes in mechanical properties. Optical and X-ray orientation factors of the swollen cottons are related, but the relationship differs from that of raw cotton. Birefringence indicated a reduced crystallite orientation with swelling, while increased orientation was indicated by X-ray. Increases in strength were almost linearly related to increased birefringence, and were greater for caustic soda than for ethylene diamine treatment at comparable levels of birefringence. Caustic soda treatment also decreases

crystallinity more than does ethylene diamine treatment. Dynamic modulus from tensile behaviors taken at low strains best characterize the treatments. At high strains, near rupture, dynamic modulus is essentially constant for all treatments studied. Crystallite orientation was best observed in the initial slopes of the dynamic modulus vs. static strain curve.

A study of the effect of caustic soda and other swelling agents on the fine structure of cotton is continuing under a P. L. 480 grant at the Shirley Institute, Manchester, England. The effect on the fine structure of scoured Acala 4-42 cotton of treatment with 5-normal sodium hydroxide at different temperatures followed by washing at different temperatures and drying by various methods was investigated. X-ray diffraction, infrared-deuteration, moisture sorption, acetylation, stress-strain curves, and optical and electron microscopy provided data to show effects of treatment variables. Strength was essentially unaffected under any of the conditions, but improvements in water retention and reactivity in nonswelling and swelling reagents were markedly dependent on the choice of correct conditions of swelling, washing, and drying. Other swelling agents studied were sodium ferriartrate, and sulfuric and phosphoric acids of various concentrations. The chief conclusion was that their mode of action and effect on the fine structure is different from that of caustic soda. High interfibrillar swelling occurred in many of the solutions, without a lattice change in the final product but with improved reactivity to both nonswelling and swelling-type reagents.

5. Relationship of Gross Structure of Cotton to Behavior of the Fibers in Textile Structures. In completed grant research at Georgia Tech Research Institute, an instrument was designed to establish frictional characteristics of cotton fibers. Studies of the variables in testing demonstrated that the friction profile showing slip-stick forces was more informative in characterizing the cotton fiber surface differences than was the median frictional value. Friction profiles for fourteen different cottons showed that the greatest differences among cottons occurred in the frequency and magnitude of forces for points of high and low frictions. These points are caused by fiber surface abnormalities, convolution angle at reversal, and cell wall damage. Coefficients of friction and friction profiles change as cottons pass through various stages in mechanical processing from boll to yarn. Processing removes some abnormalities but increases others, such as fiber surface damage. During processing, the maximum changes in frictional coefficients occur at the spinning frame.

6. Methods and Instruments for Measuring the Physical Properties of Cotton and Its Products. Research is being conducted to correlate abrasion tests with service wear of durable-press cottons. Laundering tests in home-type equipment to evaluate durable-press cotton trouser cuffs made from fabrics of different weights and constructions showed that type of load (mixed or separate) was not a factor in abrasion damage. However, longer time in the dryer increased the abrasive damage for all constructions.

Use of fugitive softening agents, such as glycerine, or of a presently available commercial laundry softener in the rinse water gave little or no reduction in edge abrasive wear. Durable-press trousers and shirts fabricated from these same fabrics are presently undergoing service wear tests.

A fundamental investigation of the geometry of wrinkles as they affect the rating of acceptability of wash-wear cotton fabrics is being conducted in a P. L. 480 project at the Institute for Fibres and Forest Products Research, Ministry of Commerce and Industry of the State of Israel. Parameters describing the height, sharpness, and density of wrinkles on the surface of a fabric have been defined and procedures to measure these parameters have been developed. With the aid of slit illumination, contour lines are formed on the wrinkled fabric surface and are traced and measured by the use of electronic analog computers. Wrinkling varied for different fabric constructions; these results agree with visual appearance tests. Determination of the relative importance of each parameter and the effect on fabric appearance is continuing.

The utility of optical techniques for determining the presence of small tangled masses of cotton (neps) was demonstrated in contract research at Stanford Research Institute, South Pasadena, California. Light scattering from cotton caused by reflected or transmitted light was measured and found adequate for establishing the presence of neps and trash particles in cotton. A novel method was developed for opening raw cotton without creating fiber entanglements. The research has resulted in the development of a prototype instrument for counting neps.

The same contractor (Stanford Research Institute) also conducted exploratory research to aid in selecting the basic principle and operating components of an instrument to determine fiber length distribution. An optical technique based on measuring the forward scattered light from cotton fibers illuminated in a high-speed air stream appears feasible. The prototype model was designed and some subassemblies of components were checked out, but continued delay in delivery of certain optical parts has prevented completion of the instrument. Successful development of such an instrument will help geneticists to develop cotton with desired length, machinery manufacturers to improve ginning and textile equipment, and textile mills to produce higher quality cotton products.

An investigation of the mathematical and theoretical aspects of the relationship between the fiber length distribution of cotton specimens before and after sample preparation has been continued in a P. L. 480 project at the Lodz Polytechnic College, Lodz, Poland. Coordination has been worked out in both approach and mathematical notation between this investigation and research recently reported at the Southern Division. Data from the Division's research have been generalized and amplified by use of a probability function that permits evaluation of a wide variety of breakage models. An apparently new technique for direct measurement of fiber extent ("projected length" in U. S. terminology) was developed and evaluated. However, this

technique is presently tedious, requiring removal of individual fibers from roving as a plate is moved in 2 mm. intervals. When a fiber arraying technique developed in Russia was applied and the results compared with those obtained on the same cotton by a U. S. technique, there was fairly good agreement in values.

B. Chemical and Physical Investigations to Improve Products

1. Exploratory Chemical Modification and Finishing of Cotton. Increased wet wrinkle resistance has been imparted to cotton fabrics by treatment with non-nitrogenous agents such as dipotassium 1,2-disulfatoethane or triphenylsulfonium chloride. An extremely rapid method has been developed for graft polymerizing glycidyl acrylate onto cotton. This agent has previously been shown to impart increased dry and wet wrinkle resistance to fabric. Cotton yarn converted to chlorocellulose by reaction with thionyl chloride was shown to be somewhat rot resistant. In other exploratory work, the crosslinking of cotton was achieved by treatment with sodium hydrogen maleate in the presence of zinc nitrate as catalyst. Fabrics with high wrinkle recovery were obtained by the deferred curing of grafted ethyl acrylate-N-methylolacrylamide copolymer or glycidyl acrylate homopolymer formed in situ in phosphorylated cotton fabrics.

A rapid new technique--the Differential Scanning Calorimetric method--is being used to screen potential reversible crosslinking agents for cotton. In cooperative research with the Cotton Producers Institute, application of this method to the measurement of the rates and activation parameters for the thermal dissociation of cotton crosslinked with dicyclopentadienedicarboxylic acid has demonstrated the pronounced effect of solvents and trapping agents in the system. Results from the kinetic study correlated well with swelling, as measured by fiber width. Investigation of the internally catalyzed crosslinking of quaternized aminoethylated cotton fabrics with divinyl sulfone and with bis(2-hydroxyethyl)sulfone showed that a thermal treatment of the crosslinked fabrics produced high wet and dry wrinkle recovery. This system offers potential for combining thermally reversible creasing with delayed curing to produce a more desirable durable-press product.

By use of vacuum thermogravimetric analysis, information was obtained on the kinetics of the thermal dissociation of aryl carbamylated cottons. The results indicate that steric factors in the carbamate molecule are very important in its thermal dissociation. In general, N-aminosubstituted phenyl- and N-pyridyl carbamylated cottons undergo thermal dissociation more readily than do methoxy- or methylthio-substituted-phenylcarbamylated cottons. Unsubstituted N-phenylcarbamylated cottons were found to contain cellulose N,N'-diphenylallophanate as well as cellulose N-phenylcarbamate. The presence of both allophanate and carbamate linkages in these cottons may help to explain the poor reversibility of crosslinks introduced into cotton by difunctional isocyanate-generators, since the allophanate linkages dissociate more slowly than do the carbamate linkages.

In grant research at Textile Research Institute, Princeton, New Jersey, aromatic substituents were introduced into cotton by a transesterification reaction. Because this reaction produces byproducts that do not degrade cellulose, it may offer a more promising route than direct esterification with acid chlorides for the introduction of substituent groups that impart thermoplasticity. However, the products obtained by reacting cotton with several difunctional aromatic compounds were completely unstable in water; this unusual behavior needs further examination. Cotton in the form of sodium cellulosate was modified with acrylonitrile by anionic graft polymerization. This technique produces grafted cottons with very high degrees of substitution and with polyacrylonitrile side chains of relatively low molecular weight, the two structural characteristics that appear to be needed to impart thermoplasticity to cotton.

Unmodified cotton and cottons containing amino groups as built-in catalytic sites have been reacted with heterocyclic compounds containing the oxirane or thiirane group and with acid anhydrides. Cottons chemically modified to contain acidic and basic groups have been treated to impart ionic crosslinks. By use of such in situ catalysis, it is possible to produce chemically modified cottons whose properties differ from those imparted by a given reagent in the presence of an external catalyst.

In exploratory research conducted in cooperation with the International Lead Zinc Research Organization, a number of selected lead and zinc compounds were found to impart to cotton such properties as rot, mildew, and flame resistance. Cotton fabrics treated with lead and zinc salts, such as N-(tributylplumbyl)imidazole, zinc pyridinethiol N-oxide, triphenyllead laurate, and tributyllead acetate, exhibited good rot resistance, retaining 100% of their breaking strength after 10 weeks of soil burial. Fabric treated with thioethyltriphenyllead retained 100% breaking strength after 16 weeks of soil burial. Application of a resin binder and rutile titanium dioxide with an organolead compound enhanced the weatherability of the fabric. In addition, these compounds inhibited mildew and algae growth. Combinations of lead and sulfur compounds, such as lead sulfosalicylate, were found to impart good nondurable flame resistance to cotton fabric. Inexpensive zinc salts, such as zinc borate and zinc phosphate, imparted semidurable flame resistance.

Contract research is in progress at Bjorksten Research Laboratories, Madison, Wisconsin, to investigate the effect of resin thermoplasticity or thermosettability on the resistance of treated cotton fabrics to abrasion. Two sets of factorial experiments have permitted evaluation of how abrasion resistance is influenced by several variables, including two fabric structures, three monomers at several levels of add-on, and two cross-linking resins for grafting substrates. It was found that glycidyl acrylate can be grafted to cotton without opening the epoxide ring, which remains available for subsequent reaction. When selected thermoplastic resins were chemically grafted to cotton and then thermosetting resins were applied, the abrasion resistance of the treated fabric was almost equal to that of

the untreated control. Work is now aimed at the development of a resin that has both thermoplastic and thermosetting properties.

In contract research at New York University, exploratory experiments were conducted to optimize reaction conditions for vapor phase encapsulation of cotton fibers by two approaches: (1) addition polymerizations of vinyl-type monomers, and (2) interfacial vapor-liquid condensation polymerization of polyamides. Work is continuing on the vapor phase polymerization of polyamides with emphasis on the preparation of crosslinked polyamide polymer coatings. Microphotographic examination of various polymer coated fibers prepared by vapor phase methods was also carried out to gain some insight into the physical nature of the polymer deposits. Initial growth of the polymer on the cotton substrate appears to be controlled by the substrate, and the deposits are relatively continuous and smooth. At higher levels of add-on, the deposition becomes less surface-controlled and increasingly irregular growth takes place.

In contract research at Harris Research Laboratories, Rockville, Maryland, conventional durable-press treatments were modified to decrease the drying time of cotton fabrics. The drying time of these treated fabrics was 66% less than that of untreated cotton and 45% less than that of conventional durable-press cottons. The modifications involve either pretreatment or aftertreatment of the fabric with polymeric film-forming agents. Pretreatment with a crosslinked, slightly hydrophobic agent, such as a peroxide-crosslinked vinyl chloride-alkyl acrylate copolymer or after-treatment with a highly hydrophobic agent, such as a long-chain N-methylolamide water repellent, appears preferable. The method is applicable to a standard pad-dry-cure durable-press treatment or to the wet-fixation process. The polymers, used in concentrations of 0.35-5.0%, are deposited around the individual fibers of the fabric.

2. Chemical Reactions Initiated in Cotton Cellulose and Chemically Modified Cotton by High-Energy Radiation, Light, and Heat. Conditions for radiation-activated reactions of cotton to obtain high radiochemical yields of products were developed in a recently completed project. In particular, vinyl polymers of a wide range of molecular weights were grafted onto cotton to give new textile products, some of which possessed improved abrasion resistance and other desired properties.

Graft copolymers of cotton, prepared by free radical initiated processes, are being evaluated for their durable-press properties. Preliminary results indicate that it may be possible to make a satisfactory durable-press product by grafting onto cotton a monomer such as acrylonitrile or certain alkyl methacrylates, and then treating with a commercial durable-press crosslinking agent. The experimental fabrics produced by this method had higher abrasion resistance and wrinkle recovery than did control fabrics. Progress was also made in obtaining a better understanding of free radical reactions of cellulose initiated by hydroxyl and hydroperoxy radicals as related to graft copolymerization reactions. In other work,

high-energy transfer studies showed that the presence of either electropositive or electronegative substituents on the aromatic rings of esters of methyl D-glucopyranoside did not affect significantly the radio-protective effects of the aromatic groups. This suggests that similar derivatives of cotton cellulose would be resistant to radiation damage.

The Cotton Technological Research Laboratory, Bombay, India, has continued its investigation of the preparation of radioresistant and radiosensitive celluloses under a P. L. 480 grant. Cottons chemically modified by acetylation, benzylation, benzoylation, and acrylonitrile grafting to various degrees of substitution were prepared. These cottons were exposed to gamma irradiation at equal dosages and their physicochemical properties determined. Maximum degradation was found in the untreated cotton followed in decreasing order by the acetylated, the benzylated, and the benzoylated cottons. The data obtained verified published reports that benzoylation of cotton cellulose affords protection against the degradative effects of high-energy irradiation in proportion to the degree of substitution attained in the chemical modification.

3. Mechanisms, Rates and Catalysis of Reactions of Cotton Cellulose and of Chemically Modified Cotton. Fundamental studies of the mechanisms of etherification of cotton with various N-methylolureas are being made as a basis for improving delayed-cure durable-press processes. Rates and mechanisms of the reactions of cotton cellulose with selected N-methylolureas at low and high temperatures in the presence of metal salt and mixed catalysts were determined. The influence of the structure of dimethylolated cyclic ureas on reaction rates and fabric properties was investigated. Some progress was also made in correlating changes in absorptivity of a water band in the infrared spectra with changes in conditioned wrinkle recovery of fabrics finished with certain N-methylolated ureas.

The mechanisms by which dry and wet crease recoveries are imparted to cotton fabric by reaction with monobasic acids were elucidated and the characteristics of the acid group required to produce resiliency were delineated. The basic information about ways to improve the crease recovery of cotton other than by use of difunctional reagents could be of future value in the textile industry. In particular, the evidence that the presence and removal of a particular kind of water bound to cotton are related to crease recovery properties of the chemically modified cottons should lead to new avenues of research. Although this research has identified the types of groups needed to impart dry crease recovery for cellulose esters only, the findings should be applicable to cellulose ethers or to types of resin deposits needed to impart crease recovery to cottons.

A fundamental study of the oxidation of cotton and crosslinked cotton by hypochlorite, hypobromite, and other agents commonly used in bleaching of cotton products is continuing under a P. L. 480 grant at the Institute for Fibres and Forest Products Research of the Ministry of Commerce and Industry of the State of Israel. In further research on the mechanism of bleaching of

cotton, it has been shown that an inverse relationship exists between the adsorption of bromine and the extent of oxidation. The sorbed bromine appears to protect the cotton from oxidation by the bromine. The stabilizing against chemical attack afforded by crosslinking agents appears to be dependent upon the nature of the agents themselves. The rate of oxidation, aldehyde content, and yellowing were different in swollen crosslinked cotton. Sodium hypochlorite oxidation was nonselective in the different carbon positions in the anhydroglucose unit. Mild peroxide oxidation occurred mainly at the 3-position, producing keto celluloses. It also caused lower yields of functional groups, less degradation and yellowing, and lower amounts of aldehyde and carbonyl groups, and alkali solubilities.

4. Soiling of Cotton Textiles. In grant research at the University of Arizona, the observation of fabric soiling in situ was greatly improved by use of a scanning electron microscope. With this instrument, depth of focus and size of area viewed are much greater than with a conventional nonscanning electron microscope. Electron scanning studies of artificially soiled soil-resistant finished cotton fabrics showed the distribution of the soil within the fabric and yarn structures and on the fiber surfaces. Evidence of the soil-resistant finishes was also discernible on the fiber surfaces. Construction is in progress on a column designed to permit electron scanning of a square-centimeter area of fabric with the electron probe used to identify the chemical nature of the contaminant soils.

5. Exploratory Physical Investigations of Native and Modified Cotton. Research on the relation of fiber properties to fabric behavior in chemically treated cotton has shown that several variables in fiber and fabric structure and chemical and physical properties affect the properties of wash-wear (durable-press) fabrics. Treatments that increase the durability of durable-press fabrics have been found. The most effective procedure for increasing fabric durability consisted of slack mercerizing, treating with resin, and then curing the fabric while the tension in the warp and filling directions was held to a minimum. Stretching increases strength but decreases elongation. The effects of stretching are greater on the slack mercerized than on the scoured fabrics. Slack mercerized fabrics stretched during the cure had only small increases in durability over those of scoured fabrics. Optimum mercerization--double mercerization, if needed--was found to produce differences between treatments that were undetected if single mercerization was used. As an example, the superior native cottons reflect more clearly their superiority in the slack mercerized products.

It was found that the measurement of energy-to-break in durable-press fabrics was inadequate for predicting wear life of these materials as determined in home laundry equipment. Other work showed that the small decrease in filling strength caused by inserting a warpwise crease in durable-press garments is apparently not a major factor in the wear life of the garments.

Research has been initiated to investigate mechanisms of achieving smooth drying and abrasion resistance of cotton fabrics from changes in fiber and fabric properties resulting from various chemical treatments. In the initial phase of the work, the required cotton yarns and fabrics are being treated with selected permanent-press finishes.

The mechanism of crease formation and recovery in ease-of-care treated cotton fabrics is being investigated in a P. L. 480 project at the Swedish Institute for Textile Research, Gothenburg, Sweden. Basic research on fiber and fabric rheological characteristics indicates that both fiber crimp and fabric stretching are factors in elastic behaviors. Crosslinking when moisture is present rather than when the fiber is dry provides a better balance between tensile and recovery properties. Fabrics of different crosslinking treatments differ in their sensitivity to moisture during wrinkling and recovery. Creases made when the fabric is in an unstable moisture condition have the least recovery. For polymerization and crosslinking, the balance between tensile and recovery properties was best when crosslinking was carried out with N-methylol methacrylamide in the presence of isoprene. The results indicate possibilities of rubberlike grafts to provide wash-wear without strength losses.

Research has continued under a P. L. 480 grant at the Shri Ram Institute for Industrial Research, Delhi, India, to investigate the correlation between several important physical properties of cotton apparel fabrics and their performance in actual service tests. Two statistically designed service wear trials have been completed under controlled conditions of laundering and wearing. These included a pilot service wear trial of shirts for school boys and a service wear trial of uniforms (shirts and pants) for labor personnel. The abrasion performance of the garments in both wear trials correlated well with laboratory flex abrasion tests. Tear performance in wear was best predicted by laboratory tensile strength tests. The wear life of 3/1 khaki drill work pants used in the wear trials was improved considerably by fabricating them with the reverse side of the fabric out. Substantial improvements in wear life were also obtained with a special "built-in-lubrication" finish developed at the investigating institution. Three additional wear trials involving fabrics specially finished for soil resistance, crease resistance, and built-in lubrication for improved wear resistance, have been initiated.

In other P. L. 480 research at the Shri Ram Institute for Industrial Research, experiments with urea-formaldehyde treated cotton fabrics have demonstrated that countercurrent fluidization techniques for curing the resin may have advantages over conventional curing methods through the higher heat transfer rates achieved. This technique, however, was not found to afford improvement in product quality. In comparison with conventional curing, countercurrent fluidization curing afforded a slight improvement in crease recovery angle at equal resin fixation but caused commensurate loss in tensile strength. Tearing strengths were relatively unchanged. Achievement of suitably high levels of solids holdup in the

fluid bed without column flooding and subsequent bed collapse has been identified as the main problem retarding further development of the countercurrent fluidization curing technique.

A basic investigation of the behavior of cotton fibers when subjected to aerodynamic forces is now nearing completion in a P. L. 480 project at the Chalmers University of Technology, Gothenburg, Sweden. A specially designed wind tunnel for studying the parallelization of fibers in high-velocity air flows was constructed in which the walls of the mid-section and the cross-sectional area of the outlet are adjustable. By use of high-speed, stroboscopic picture techniques, the paralleling effect of fibers at varying cone angles, lengths, and air velocities were studied. Evaluations were made by counting and comparing the number of fibers parallel, with leading hooks, trailing hooks, approximately 45° incline and approximately 90° incline in both the upper and lower parallelization zone. The results showed that parallelization of air-suspended fibers in high-speed air is possible in conical channels, and that parallelization is more sensitive to increases in air velocity than to variation in cone angle. With a constant cone angle the paralleling effect increases significantly as air velocity is increased from 10 to 100 m./sec.; however, the effect reaches a maximum at 30° cone angle.

In research under a P. L. 480 grant at the Juan de la Cierva School of Technical Investigations, Barcelona, Spain, twenty-three cottons differing only slightly in length but widely in Micronaire reading and Pressley strength were studied to determine the effect of fiber properties upon drafting tenacity at the spinning frame. By use of the method devised to determine yarn strength between the front roll and pigtail, the strength of the partly spun yarn was compared with the yarn on the bobbin. When fiber length alone was correlated with drafting tenacity, the mean of the 60% longest fibers gave the best correlation. When the ratio of length to Micronaire reading was used, the mean length correlated best. For the partly spun yarn, yarn tenacity varied inversely with tex; for the yarn from the bobbin, the opposite was true.

A study of the factors that affect drafting capacity, spinning efficiency, and yarn quality of the direct sliver spinning system was continued under a P. L. 480 grant at the Ahmedabad Textile Industry's Research Association, Ahmedabad, India. Two cottons were selected for studying the effect of spinning draft on yarn quality for both the OMS direct spinning system and the shortcut system (roving and SKF spinning system.) These were a short staple Indian (Wagad) cotton for spinning 13/1 to 16/1 counts and a 1-5/32" California cotton for counts 36/1 to 44/1. In both the OMS and SKF spinning systems, the optimum spinning draft for the Wagad cotton depended on yarn count. Skein strength decreased with increase in draft from drawing through spinning. In both systems, however, the spinning draft to achieve maximum skein strength for the California cotton increased with increase in draft from drawing through spinning.

Research is in progress under a P. L. 480 grant at the South India Textile Research Association, Coimbatore, India, to investigate the effects of atmospheric conditions during the spinning of cotton yarns on yarn properties and spinning efficiency. Limited evaluations have been made involving one cotton, two yarn counts, each spun with two twists, two drafts and two spindle speeds, with spinnings performed under two levels of relative humidity and four levels of temperature. All appropriate evaluations of the resultant yarns have been made. Results so far indicate that increases in temperature up to 91°F, rather than increases in relative humidity, have the greater effect in increasing ends down during spinning. However, at this temperature (91°F) breakages increase with increases in humidity. Moreover, the adverse effects of higher spindle speeds, drafts, counts, and lower twist factors on end breaks are accentuated by an increase in temperature.

In a P. L. 480 project at the Ahmedabad Textile Industry's Research Association, Ahmedabad, India, research is being directed toward the development of a stochastic model for determining the efficiency of drafting independent of the size of fibrous strands. In initial work, a theoretical distribution describing the distribution of distances between fiberlike ends was assumed to be of the gamma-type. The correlogram of this distribution was compared to an empirical distribution obtained using the Uster tester and was found not to fit. A decision was made to try an anomaly of the damped harmonic type to describe the distribution. Methods for estimating the spectrogram of this distribution have been selected.

Fundamental investigations to obtain information needed to predict the performance of cotton yarns during weaving have continued under a P. L. 480 grant at the Fiber Research Institute, T.N.O., Delft, Holland. Theoretical approaches have indicated that end breakage during weaving is due to repeated stretching of the yarns, which causes abrasion failure, and to tensing effects on the yarns, which cause rupture at "weak spots." Preliminary work has been done to relate weaving tension to a number of weak spots and to end breaks during weaving. Laboratory equipment has been developed to simulate the dynamic stresses applied to yarns under actual weaving conditions. A relationship has been developed between the weak spots of unslashed and slashed yarns since most cotton yarn is used in the latter condition. Experimental data thus far indicates that only some of the end breaks during weaving are caused by weak spots. Studies are being continued to determine the other contributing factors.

C. Technology--Process and Product Development

1. Improved Procedures for Mechanical Processing of Cotton. Research was initiated to develop optimum textile processing techniques, blends, and products for increasing the utilization of low and high Micronaire reading cottons of medium staple length. Cottons with Micronaire readings ranging from 2.8 to 5.5 and classer's lengths of 1-1/16" and 1-1/32" were obtained,

and the relevant fiber properties were measured. During this assessment, the ratio of fiber amount to beard weight was found to be highly correlated with the Micronaire reading, a relationship that may be useful to industry in estimating the Micronaire value of a particular cotton. Further investigations will be conducted on the ratio of fiber amount to beard weight in relationship to other fiber properties, yarn properties, and end breakage in spinning.

To complement this intramural research, similar research was recently initiated under contract at Texas Technological College, Lubbock, to increase the utilization of low and high Micronaire reading cottons of the shorter staple lengths.

In further research to determine the interaction of processing variables with yarn properties and end breakage, evaluation of drawing frame variables showed that for standard draft distributions, spinning efficiency and yarn properties were improved when the back rolls were opened and the top second roll was raised. These drawing frame settings, which are standard for processing combed stock, may thus also be applicable to the processing of medium staple carded cottons. For experimental draft distributions, however, use of closed back rolls and raised second top roll improved yarn uniformity, reduced yarn imperfections, and increased yarn strength. The new technique for determining projected mean length has now been used successfully by a large cotton textile organization; its adoption by industry will aid in lowering the cost of cotton products.

A guide has been provided cotton breeders indicating that efforts towards increasing fiber bundle elongation beyond present levels might not provide sufficiently significant improvements in processing performance or end product quality to overcome associated agronomic problems of yield, low fiber strength, maturing season, etc. Independently of staple length, high elongation fibers produced high elongation yarns; therefore, since there are trends toward high spindle speeds and high yarn tensions, which reduce yarn elongation, the textile industry can realize advantages by using high elongation cottons, especially for knitting yarns. The effect of differences in fiber bundle elongation behavior during spinning has been determined for medium and short staple cottons. This information, which was obtained in contract research at Auburn Research Foundation, Inc., will aid the textile industry in selecting cottons suitable for specific end products, at lowest costs for raw material and processing.

2. New and Improved Mechanical Processing Machinery--Opening Through Carding. An automatic control system has been developed to enable the SRRL Bale-Opener-Blender to maintain uniform production rates and tuft size, regardless of bale density and irregularities in loading. The need for periodic inspection of processing cylinder pressure and for manual adjustment to maintain desired production rates has been completely eliminated. Extensive mill tests have shown that the BOB can replace seven machines in a three-picker opening line and produce equal or, in many respects, better quality stock for subsequent

processing. One firm has applied for a license and will produce the machine. Three other firms are investigating its possible production.

A recently developed mechanism, the Lap Drafter, appears capable of upgrading yarn produced from low-grade cottons that are difficult to process. When picker lap was processed through the Drafter and its accompanying apparatuses for opening fibers and removing short fibers, yarn strength was improved as much as 8% and yarn imperfections were reduced 20%. However, yarn quality was not improved when high Micronaire cotton was processed; therefore, the additional manipulation is beneficial only with certain cottons. However, availability of such a mechanism will boost the utilization of the part of the crop that is normally sold at a discount.

A new machine to individualize fibers has been designed, utilizing a special type of wire teeth and optimum speed ratios to permit cotton to be carded from roll to roll without having the rolls load. Since no stripper rolls are needed, the opening mechanism is simplified and fiber damage is minimized. Individualizing fibers from rawstock without damaging them is a prerequisite for the development of a radically new method for producing higher quality cotton textiles at lower cost. It is one of the most difficult and perhaps the most important problem in research on the mechanical processing of cotton.

Recent experiments with cotton in electrostatic fields have entailed study of the relationship of the moisture content of fibers to their physical behavior in electric fields as well as investigation of the variation in activity of fibers transformed from a nonconductive to a conductive state. In another phase of the work, most fiber properties were not appreciably affected by ozone or electrostatic treatment. However, electron microscopy revealed that the surface structure of the treated fibers differed slightly from that of the control. Differences among the ozone-treated samples were substantiated by the alkali-centrifuge test, whereas changes detected by this test for the electrostatically radiated samples were insignificant. Future work will emphasize the application of basic findings to the development of prototypes that will electrostatically align airborne cotton so that it can be subsequently formed into a textile strand.

3. Durable-Press Cotton Products. Several variations of the wet-fixation process of the National Cotton Council were shown to be promising processes for durable press. Fixation overnight at room temperature or fixation by heating in the presence of an inert additive produced wrinkle-resistant fabrics with relatively high abrasion resistance. Properties were improved by use of lower amounts of reagent and lower add-ons than previously reported for the standard fixation procedures. In simplified, one-step fixation procedures for production of pre- and postcure durable-press cottons, steaming under pressure was used for efficiently fixing melamine resin-crosslinker combinations on the cotton. These simplified procedures require only one-third the amount of chemicals normally used for wet fixation and do not require a wash step. The durable-press fabrics produced exhibit

about the same wrinkle recovery, abrasion resistance, and smooth-drying properties as those produced by the original wet-fixation process. If the simplified procedures can be successfully carried out in plant equipment, chemical and processing costs will be comparable to those of a pad-dry-cure treatment.

The easy-cure process--a new technique in which cotton impregnated with a dimethylol carbamate agent and hydrochloric acid is made wrinkle-resistant by drying and curing at low temperature--was successfully carried out on a semipilot plant scale; thus, the process appears to be amenable to adaptation for continuous, plant-scale processing. A procedure was also devised for producing durable creases in cotton finished by the easy-cure process. The ability to introduce these creases could provide another route to permanent-press garments. Since the finish has been fully cured and washed in the easy-cure processing step, the new techniques developed in this research may overcome the problem of formaldehyde release from fabric sensitized with carbamate agents for subsequent processing by the conventional postcure method. Furthermore, the appearance of the creases and the smoothness of the finished fabric are as good or better after line-drying as after tumble-drying.

Crosslinking cotton in a partially swollen state did not by itself improve abrasion resistance. However, results show that the contribution of swelling toward abrasion resistance in modified crosslinking treatments is of a complementary nature. In cotton crosslinked at various degrees of swelling, abrasion resistance varied inversely with wash-wear performance. Noncrosslinking substituents such as the hydroxyethyl group introduced into swollen cotton before a dry-cure crosslinking treatment are as effective as crosslinking substituents for improving wet wrinkle recovery and spin-line dry wash-wear ratings. Active catalyst mixtures from a hydroxy acid and a metallic salt can be made from a wider range of salts than believed previously. The organic acid component may be one of many alpha hydroxy or alkoxy carboxylic acids. Carboxyl groups introduced from hydroxy acids in catalyst mixtures improved the soil release properties of crosslinked cotton. Solvent application of agents to cotton for dry-cure crosslinking gave properties about equivalent to those obtained by water application.

Low-density, emulsified polyethylenes of molecular weight ranging from 16,000 to 24,000 were found to crosslink readily as a film on the fibers of cotton fabric--a finding of considerable importance since polyethylene used even as an auxiliary agent increases the tearing strength, wrinkle resistance, and softness of durable-press cotton fabrics. The crosslinking of cotton by alpha, beta-unsaturated esters and amides has now been shown to proceed under acid catalysis; this result may lead to new durable-press processes that avoid the yellowing and oxidation caused by base catalysis. Another durable-press treatment, which utilizes dimethyl silicone, benzoyl peroxide, and N-methylol agents in the absence of cellulose crosslinking catalysts, was made more feasible economically by use of an inexpensive polymer as an extender for the silicone. In other research, a rapid method

for fixing dyes on cotton by deposition of crosslinked dye polymers was recently developed and may lead to a technique for applying dyes that are resistant to the abrasive frosting of durable-press fabrics.

A one-step pad-dry-cure process has been developed for applying a crosslinking agent and a polyurethane additive to cotton to produce abrasion-resistant, durable-press goods. Good durable-press performance has also been achieved using a variety of polyether additives (glycol coreactives) with crosslinking agents. By proper selection of additive, it is possible to obtain durable-press fabrics that possess good soil release characteristics, or absorb optical brighteners and dyes, or have specific types of wrinkle recovery properties. Use of urea or thiourea in combination with a crosslinking agent in one-step finishing has given a combination of acceptable wrinkle recovery performance and high retention of breaking strength. With cotton goods that possess a reasonable amount of smooth-dry performance before chemical treatment, such as knits, seersuckers, or corduroys, crosslinking in the swollen state appears to offer a combination of acceptable appearance and sharply improved physical properties. Grafting of block copolymers of polyethylene oxide and polypropylene oxide has produced fabrics with improved wrinkle recovery and tear strength.

Polymer emulsions were used successfully for the dual purpose of sizing yarns and improving fabric properties such as breaking strength and abrasion resistance in durable-press goods. Yarns sized with cold mixtures of polyurethane and polyvinyl alcohol (PVA) or polyurethane and carboxymethylcellulose (CMC) could be woven more efficiently. Desizing of the PVA or CMC does not strip the polyurethane from the yarn.

In studies of the blending of treated and untreated cotton fibers to improve the abrasion resistance of durable-press goods, the use of unscoured, unbleached rawstock was investigated as a means of improving mechanical processing and reducing cost. However, when such rawstock was treated with resin and blended with the untreated stock in a 50/50 proportion, the resulting fabrics did not have acceptable durable-press characteristics.

Satisfactory progress has been made in the contract research at Fabric Research Laboratories, Dedham, Massachusetts, to improve the dimensional stability of durable-press fabrics made from blends of resin-treated and untreated cotton fibers. It was found that scoured and bleached rawstock can be successfully treated with resin at a reasonably high production rate by use of a wool scouring train. Yarns made from a 50/50 blend of untreated and resin-treated fibers have been spun, and some of the fabrics have been woven.

The inclusion of softeners and other additives in either or both steps of the polyset durable-press process for cotton fabrics has greatly enhanced the fabrics' wrinkle recovery, with good retention of other physical properties. By use of only the first step (polymer deposition), the

abrasion resistance and wash-wear appearance of treated broadcloth and sheeting fabrics have been significantly improved. This one-step version of the polyset process utilizes zinc acetate with or without zinc nitrate as the catalyst, a polyethylene softener, and a polyurethane to coat the outside of the fibers. The one step makes the process more practical, particularly for producing precure durable-press goods, such as piece goods and sheets.

The large loss in breaking and tearing strength usually produced in cotton fabric by durable-press treatment followed by repeated laundering has been almost entirely overcome by weaving the fabric from yarn that was mercerized slack and restretched to 100-103% of original length. It is feasible to use vat dyes, reactive dyes, crosslinked silicones, or polyurethanes in conjunction with wash-wear finishing of these fabrics. The frosted or whitened appearance caused by repeated laundering of cotton wash-wear or durable-press garments made from vat-dyed fabric has been largely overcome by employing reactive dyes instead of the vat dyes. In contrast to the vat dyes, which do not thoroughly penetrate the fabric and dye all of the fibers, the reactive dyes produce an even color throughout the fabric. Consequently, worn areas are much less visible. Application of this finding should increase the use-life of dyed fabrics.

It has been demonstrated that abrasion resistance can be improved by slack mercerization and by filling compaction; elastic recovery properties of stretch fabrics can be improved by modifications of yarn and fabric structure; and the wear life of wrinkle-resistant, durably creased cotton garments can be increased by preferential crosslinking treatments.

Three techniques for preferentially applying crosslinking resins to selected regions of fabric structures have been developed. Two techniques, (1) coating the back of the fabric with a viscous solution containing the crosslinking reagent, and (2) impregnating fabric with a crosslinking agent, drying, then applying a catalyst inactivator to the face of the fabric, produce fabrics that after curing have essentially the face of untreated cotton. A third technique developed consists of backcoating with a durable-press resin followed by a light face-coating resin application. Preferentially crosslinked fabrics have satisfactory crease sharpness and smooth drying properties but less muss resistance than desired. These techniques can have a practical application for commercial finishers.

Durable-press cotton fabrics with improved physical properties were obtained by blocking the most accessible sites before crosslinking, by treating with surface polymer systems, and by mechanically compacting in the filling direction. When the most accessible hydroxyl sites on the cotton cellulose were chemically blocked by partial acetylation and then partially saponified prior to a low-level crosslinking treatment, the finished fabric had improved wet wrinkle recovery. Of the surface polymers investigated for crosslinking systems employing ammonium zirconyl carbonate pretreatments, a particular polyurethane gave the best results. Mechanical compaction of

printcloth in the filling direction to achieve 11.25% shrinkage considerably improved elongation-at-break and easy-stretch properties of the fabric.

Contract research has been initiated by Auburn Research Foundation, Inc., to develop mechanical-chemical surface treatments for fabrics to improve abrasion resistance of durably pressed cotton garments. Preliminary experiments have indicated that mechanical and chemical treatments may supplement each other to improve abrasion resistance of durable-press cotton fabric. Among the treatments studied were pressure steaming, use of additives with steaming, modified mercerizations, and stepwise crosslinking. Steaming hydrolyzes most agents to some extent, but carbamates were quite resistant. A silicone additive produced best resistance to abrasion when applied in combination with steaming.

The all-cotton seersucker fabric developed for men's durable-press apparel in cooperation with the Cotton Producers Institute was favorably received in a recent test marketing program sponsored by the National Cotton Council. It is now being produced commercially on a limited scale. Suits made from this fabric will be marketed in the summer of 1968. This research has shown that fabric weave, fabric thread count, and yarn size have significant effects on fabric wear as determined by home laundering testing. The results indicate that the resistance of a fabric to wear is dependent in part on the combined effects of certain yarn and fabric parameters, the mobility of the yarns within the confines of the fabric's structure, and the degree of exposure of these yarns to the wearing forces. Such basic information is essential to the proper design and development of fabric structures for specific end uses.

Contrary to published reports, the methyl formcel-formic acid system for vapor phase treatment of cotton to produce durable-press properties was found to be almost nonreactive. Consequently, other potential reagents were evaluated in a series of experiments with different formaldehyde donors, temperature, time, catalyst, and concentration. Cottons treated in these experiments were judged on extent and uniformity of reaction, resiliency, and tear resistance. Although a number of products had excellent smooth drying properties and resiliency of durable-press magnitude, their tear strength was impaired. However, some important trends in the mechanisms and kinetics of the reactions were identified.

4. Weather-Resistant Cotton Fabrics. Good progress is being made in cooperative research on weather-resistant cotton fabrics with the Canvas Products Association International and the Cotton Producers Institute. In further studies of the Zirchrome Process, an add-on of 0.5% copper imparted essentially as much rot resistance to cotton fabric as did 0.9%. Treatment at the 0.5% level gave good protection to sandbags through 16 weeks of field exposure; it was more effective than 1.4% copper deposited by cuprammonium processes and as effective as 1.31% copper applied by treatment with copper naphthenate. Since the Zirchrome treatment efficiently imparts a modest degree of rot resistance to cotton and since

certain weather-resistant water repellants can be incorporated in the formulation, the combined process is useful in the production of outdoor fabrics such as tents and tarpaulins.

As previously reported, a clear weather-resistant finish based on zirconium acetate catalyst--methylolmelamine resin was also developed in this cooperative research. The excellent performance of this finish for 36 months of outdoor exposure and the results of four years' exposure of fabrics treated with a low level of mixed pigments suggest that combination of these two treatments may well yield an extremely effective low-weight finish for weather-resistant cotton fabrics. In addition, a large amount of background information on the outdoor exposure performance of fabrics treated with various finishes has been obtained. These data will be invaluable as references in controlled laboratory exposures designed to yield information about the mechanisms of degradation by light.

In research conducted under contract at the Southern Research Institute, Birmingham, Alabama, it was found that rot and abrasion resistance are significantly improved in duck and drill fabrics when they are grafted with acrylonitrile, styrene, or methyl methacrylate by the radiation initiation method. Some specimens grafted by radiation initiation retained 80-90% strength after six weeks' soil burial. Flat abrasion measurements of some grafted fabrics were considerably higher than those of untreated fabrics. The highest tensile elongation observed was in fabric grafted with styrene by radiation initiation to 15% polymer add-on. After outdoor weathering, fabrics grafted by radiation initiation with methyl methacrylate showed less degradation than those grafted with acrylonitrile or styrene, and also less than those treated by interfacial polymerization. The radiation initiation method of finishing cotton textiles has potential as a commercial method for improving mildew, rot, and abrasion resistance.

Contract research to develop improved coated cotton fabrics with optimum strength-weight characteristics for outdoor uses has continued at Fabric Research Laboratories, Inc., Dedham, Massachusetts. Coatings were applied to eight fabrics selected on the basis of their performance in the initial completed phase of the work. When the coating was applied by standard techniques, the tearing strength of all the fabrics was reduced: plain weaves, about 25%; twills, about 60%; basket weaves, about 70%. The amount of reduction depended primarily on weave rather than other construction variables. However, use of special coating techniques greatly reduced--and in some instances prevented--these losses in tear strength. Lowering the modulus of the coating also increased the tear strength, but decreasing the viscosity had no effect or a deleterious one. Lubrication of the fibers of the fabric before coating had no effect.

5. Soil-Resistant Cotton Textiles. Optimum conditions were determined for pilot-plant application of two new oil-repellent finishes: THPC-fluoroamine and a methylolated fluorourea. These treatments have better soil release and soil redeposition characteristics than do several commercial fluorocarbon

finishes. Unlike a recently introduced commercial soil-release agent, the urea finish is durable to repeated laundering and also imparts moderate water repellency to cotton. Wrinkle recovery was also achieved with each finish by formulating it with a commercial permanent-press agent. Some textile properties of the fabrics treated with such a combination are inferior to those of untreated cotton, but most characteristics are better than those of fabrics treated with the permanent-press agent alone. Although preliminary experiments indicated that a third oil-repellent finish--the ethyl perfluorooctanoate-ethylenimine emulsion--could also be applied with the permanent-press agent, more recent research has shown that the required catalyst is not compatible with the emulsion.

6. Insect-Resistant Cotton Bags. In cooperation with the Stored-Product Insects Research and Development Laboratory at Savannah, Georgia, the Textile Bag Manufacturers Association, and the Agricultural Stabilization and Conservation Service, excellent progress has been made in research to develop cotton bags designed to protect flour, cornmeal, and other milled cereals from attack by insects during shipping and storage. Results of large-scale, 12-month food storage tests have shown that tube-type cotton bags treated with insect repellent, lined with wax paper, and closed with taped-over seams are practical insectproof containers for storage of such foods. The performance of these bags was comparable to that of multiwalled paper bags treated with the same repellent. Plans are being made to evaluate similar lined cotton bags in an overseas test-shipment of cereal foods to the Philippines. Other research showed that migration of the repellent into cornmeal, evaluated in accelerated tests, was effectively retarded by use of either polymer coatings (at least 40% dry add-on from a polymer emulsion containing insect repellent) or plastic films (laminated to the fabric with an adhesive containing insect repellent) between unlined fabric and the foodstuff.

RPA 709 - REDUCTION IN HEALTH HAZARDS INVOLVED IN USE OF NONFOOD FARM PRODUCTS

A. Chemical and Physical Investigations to Improve Products

1. Synthesis of Compounds Potentially Useful for Imparting Flame Retardancy to Cotton. New aziridinyl phosphorus compounds are being synthesized and characterized in P. L. 480 research at the Hebrew University of Jerusalem, Israel, for use in conferring various desirable properties, including flame retardancy, to cotton. Eight organophosphorus tetrachlorides were synthesized. These included compounds prepared from diols, primary and secondary diamines, and alkylene diphosphonic acids. Eight new tetra-aziridinyl derivatives were prepared by reaction of the tetrachlorides with aziridine. Most of the tetrachlorides and all of the tetra-aziridinyl phosphorus derivatives were purified and identified by analysis. The relative reactivity of the various types of aziridinyl derivatives as alkylating agents was determined. The aziridinyl phosphorus compounds will

be studied as crosslinking agents for cotton textiles and are also being tested for chemosterilant and anticancer activity.

B. Technology--Process and Product Development

1. Flame-Retardant Cotton Textiles With Other Desirable Properties. The tetrakis(hydroxymethyl)phosphonium hydroxide (THPOH), ammonia-fixation process for imparting durable flame resistance to cotton fabrics has been made more attractive for commercial use by the successful substitution of aqueous THPOH for the alcoholic solution formerly employed. Successful application of this new finish to full-width fabric in pilot plant and mill trials has evoked considerable interest from industry and the military. A new approach for using THPOH on cotton was also discovered. By stabilizing THPOH-ammonium hydroxide solutions with copper salts, it was possible to apply the retardant by a pad-dry-cure procedure instead of by the usual fixation with ammonia gas, which requires special equipment.

Systems containing various flame-retardant agents also imparted other attractive properties to cotton. THPOH, methylolmelamine, and magnesium acetate catalyst imparted flame resistance, wrinkle resistance, and improved abrasion resistance. A one-step treatment based on APO and a polysiloxane imparted not only flame and wrinkle resistance but also water repellency. APO-THPC imparted the highest degree of rot resistance; finishes applied by a pad-dry-cure method were superior to those applied by ammonia curing. A method was found for incorporating thioethyltriphenyllead, a very good rot-resistant agent for cotton, into the THPOH-ammonia flame-retardant finish. This finish may have potential for treatment of outdoor fabrics.

Pad-dry-cure application of a new compound, 1,1,2,2-tetrahydropentadecafluorononyl bis(aziridiny)phosphine oxide, yielded good oil repellency and moderate water repellency, both of which were moderately durable to laundering and drycleaning. Polymerization of the aziridine adduct of methacrylonitrile on cotton fabric improved flex abrasion resistance. And several commercially available organophosphorus compounds appear to have potential as relatively inexpensive semidurable flame retardants. It is particularly important that these agents are suitable for application to fleeced cotton knit fabrics, such as sweatshirts, because at present there is urgent need for flame retardancy in such garments. Cotton twill treated to 12% add-on with a polyphosphoramid-formaldehyde-cyanamide formulation exhibited very good flame resistance, which was durable to five launderings. This finish is relatively inexpensive as compared with current flame-retardant finishes, and it appears promising for applications where semidurability is desired.

2. Flame-Retardant Cotton Batting. In cooperative research on cotton batting with several industrial associations, the performance characteristics of Cotton Flote products have been improved by the use of newly available, lower cost chemical systems. These systems contain vinyl acrylates and methylated methylol melamines and require only dilution and addition of

catalysts in the manufacturing plant. Products exhibiting a good degree of flame retardancy have been developed through the use of a urea phosphate complex in the Cotton Flote process. In addition, rawstock fibers of the type used in conventional cotton batting can be made flame retardant through the use of the same urea phosphate complex or a chemical system consisting of urea diammonium phosphate, methyl formcel, and a water-soluble acrylic polymer. Rawstock so treated can be garnetted without the problems of fiber breakage or fly frequently encountered with other treatments.

Publications - USDA and Cooperative Program

RPA 407 - NEW AND IMPROVED FEED, TEXTILE, AND INDUSTRIAL
PRODUCTS FROM FIELD CROPS

Chemical Composition, Physical Properties and Structure

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AREA 2 - COTTONSEED UTILIZATION

USDA and Cooperative Program

Location of Intramural Work	Scientist Man-Years F.Y. 1968			
	Research Problem Area			
	406	407	702	Total
Louisiana (New Orleans)	:	:	:	:
Chemical Composition and Physical Properties	8.2	6.9	:	15.1
Microbiology and Toxicology	:	:	5.9	5.9
Technology--Process and Product Development	11.2	2.2	:	13.4
Total	19.4	9.1	5.9	34.4

Intramural program is supplemented by extramural support representing (a) 0.8 SMY's at State Agricultural Experiment Stations^{1/}, (b) 2.3 SMY's at other U. S. institutions^{2/}, and (c) P. L. 480 funds in 5 countries representing 161,663 U. S. dollars equivalent per year.

^{1/} RPA 407 - All on Microbiology and Toxicology.

^{2/} RPA 406 - Chemical Composition and Physical Properties 2.0; RPA 407 - Chemical Composition and Physical Properties 0.3.

Problems and Objectives

Cottonseed products face increasing competition for markets: edible products from the oil must compete with those from other vegetable oils and animal fats, and the meal--now used chiefly as a protein supplement in feeds for ruminants--is being supplanted by synthetic urea and other sources of nitrogen. To retain these markets and to open new ones is the goal of utilization research on cottonseed. Food products must be developed to improve the competitive position of cottonseed oil and meal, to provide inexpensive protein concentrates for domestic low-income groups, and to help alleviate the worldwide protein shortage. There is also need to improve the quality and nutritive value of meal used for feeds. However, the wholesomeness of both food and feed products must be assured by controlling various undesirable natural or adventitious components. Finally, to extend cottonseed's markets beyond food and feed, research is needed to derive industrially useful products.

Specific objectives of the research are:

1. To improve processing methods to preserve or enhance the intrinsic desirable qualities of the oil and meal.
2. To develop new and improved food, feed, and industrial products.
3. To expand domestic and foreign markets for cottonseed products by tailoring them to meet consumer preferences.
4. To insure the safety and wholesomeness of cottonseed products used for food or feed.

Progress - USDA and Cooperative Program

RPA 406 - NEW AND IMPROVED FOOD PRODUCTS FROM FIELD CROPS

A. Chemical Composition and Physical Properties

1. Properties of the Oil and Fatty Acids, Including Cyclopropenoids.
Complete solubility data were obtained for additional methyl and ethyl esters of fatty acids in several solvents by applying the isopleth correlation method to scant experimental data. Complete mutual solubility data were also determined for a number of binary systems, most of which consisted of methyl or ethyl esters of unsaturated fatty acids, though three were systems of long-chain methyl ketones. Studies of mutual solubilization effects and of the crystalline compounds and solid solutions formed between closely related fatty acids and their derivatives are of fundamental importance to research on methods of separation and purification by low temperature crystallization. For example, the fact that polymorphism was not observed in any of the binary systems of unsaturated ethyl esters studied indicates that these

esters could be purified by crystallization at low temperatures. The data also constitute a basis for choosing optimum conditions for physical and chemical modification in industrial processing.

Procedures for synthesizing labeled malvalic acid esters are being devised in research conducted under a grant to Boston University in Massachusetts. Although new synthetic routes now achieve greater yield of methyl malvalate, attempts to separate it from methyl 8-heptadecynoate, which is also produced, have thus far been unsuccessful. However, some of the routes developed for the synthesis of methyl malvalate have now been modified slightly to permit the first successful synthesis of methyl stercolate from methyl stearolate. The yield of the cyclopropenoid ester was also improved. In addition, a reverse-phase chromatographic procedure was developed to efficiently separate the mixture of the cyclopropenoid ester from the acetylenic ester formed in the last stages of the synthesis. This separation is a significant contribution toward the ultimate synthesis of the desired labeled methyl malvalates.

Terminated research supported by the Foundation for Cotton Research and Education has resulted in a new process for destroying cyclopropenoids--use of a palladium-on-carbon catalyst at 150°C under hydrogenation conditions, though hydrogen need not be present. More recent research has shown that palladium chloride and palladium nitrate can also be used. These findings provide a foundation for applied work of great industrial interest, particularly since other components of the oil are not affected. Contrary to previous assumptions, hydrogenation of cottonseed oil under the usual commercial conditions does not convert the cyclopropene acid groups mostly into cyclopropanes but instead yields about ten different types of compounds, many of which are polymers and dienes. This information should be an important factor in assessing the acceptability of commercially hydrogenated cottonseed oils. Reliable techniques were developed for determining linoleates in the presence of cyclopropenes, cyclopropanes, and their hydrogenation derivatives. In related research, 2.3 grams of methyl malvalate that is 95.3% pure was prepared from concentrates from cottonseed oil.

The physiological effects of cyclopropenoids are being investigated in contract research at Ralston Purina Company, St. Louis, Missouri. Groups of young laying hens were fed rations into which one of the following oils had been incorporated at a level of 5% or 20%: soybean oil, the two Halphen-negative and one slightly Halphen-positive cottonseed oils resulting from special processing of refined and bleached oils that had originally contained 0.52% cyclopropenoids, the untreated refined and bleached cottonseed oil, and soybean oil to which Sterculia foetida oil had been added. After 48 weeks, hens ingesting the first four oils (free or essentially free of cyclopropenoids) were comparable in feed conversion and in production of eggs; in addition, their eggs were comparable in size, hatchability, and durability to storage. The eggs of hens ingesting the last two oils showed various unusual physiological effects; paradoxically, however, these deviations were less pronounced when the ration contained 20% oil. Rats

ingesting rations containing 10% of the same six oils have grown and reproduced normally, and there are no observable differences among them in mortality or occurrence of tumors after one year's trial. As an aid to this research, an analytical method was devised for estimating cyclopropenoids in animal tissues.

In a related study, removal of residual cyclopropenoids from commercial cottonseed meals by solvent extraction with a mixture of acetone-hexane-water allowed these meals to be included at the 20% level in the rations of laying hens with no detectable abnormalities in the stored eggs. This research was conducted under contract by the Illinois Institute of Technology.

Related research is being conducted under a P. L. 480 grant to the Division of Food Preservation, Commonwealth Scientific and Industrial Research Organization, Ryde, New South Wales, Australia. Study of the livers of hens whose rations contained methyl stercolate has confirmed that cyclopropenoids inhibit the enzyme systems which desaturate fatty acids. This effect was observed in all acids studied, ranging in carbon chain length from 12 to 22. Sterculic acid had greater inhibitory effect than did malvalic acid. Results suggested that there are at least two desaturase systems. The concentrations of phosphatidyl choline, phosphatidyl inositol, phosphatidyl serine plus phosphatidyl ethanolamine, and sphingomyelin were not affected. After methyl stercolate was withdrawn from the diet of the hens, the livers returned to normal activity in one week. The effect of feeding whole cottonseed or cottonseed meal to sheep, pigs, and cattle was also studied. In cattle, the ratio of stearate to oleate in depot fat was not altered; in pigs, however, the ratio was increased. Meat from sheep fed whole cottonseed had an off-flavor. It could also be detected in uncooked pork but not in cooked pork or in the meat of cattle or chickens.

2. Structure and Properties of the Proteins. In P. L. 480 research at Kyoto University, Japan, the chemical composition and reactivity of the nucleic acids present in cottonseed are being investigated. A rapid, simple, and sensitive gas chromatographic method for the simultaneous analysis of base and phosphorus composition of nucleic acids was developed. Preliminary separation of soluble RNA and high molecular weight RNA from the cottonseed kernel was accomplished. The nucleotide content of commercial cottonseed meal was lower than that of the laboratory-prepared defatted kernel. The reverse relationship was found for nucleoside and base. The content of uridine or uracil was appreciably higher than that of other bases.

Improved methods for the preparation of protein hydrolysates to permit the accurate determination of the amino acid makeup of cottonseed and other oilseed proteins are being investigated under a P. L. 480 project at the Hadassah Medical School of the Hebrew University in Jerusalem, Israel. The proteins extracted from cottonseed with 6-normal aqueous hydrochloric acid, which constituted 97% of the total protein, were subjected to proteolytic hydrolysis in an effort to induce hydrolysis without the loss

of amino acids. Various proteolytic enzymes were used, including peptidases from hog intestinal mucosa and from hog intestines, leucine amino peptidase and peptidases derived from species of parasitic protozoa. Included among the protozoa studied were species of Trypanosoma, Leptomonas, Ochromonas, Acanthamoeba, and Euglena. The influences of pH, time of digestion, temperature, and enzyme concentration were determined. Hydrolysis was not complete in any instance, but the high level of hydrolysis (93-97%) observed with T. ranarum was most encouraging.

Air-classification of defatted cottonseed flour to produce 70% protein concentrates in yields of 50% or more was shown to be reproducible and independent of seed variety and quality. A two-step extraction procedure based on the solubility characteristics of cottonseed proteins was developed for the preparation of protein isolates and has now been transferred to pilot-plant scale by a commercial food producer. This process provides two protein isolates: one composed of the low molecular weight proteins, extracted by water and precipitated at acid pH, the other composed of high molecular weight storage proteins, extracted by mild alkali and precipitated at neutral pH. The latter, the major protein isolated, is soluble in acid--an important property for use in protein-fortified beverages such as citrus drinks. The use of this two-step procedure to prepare protein isolates from alcohol-extracted glandless cottonseed flours showed that ethanol reduced the color of the acid-precipitated isolate but did not reduce the color associated with the major isolate. The manner in which the cottonseed is defatted affects the yield of protein isolates, whereas the method of isolation affects their quantity, type, and functional properties. This research was partially supported by the National Cottonseed Products Association and the Foundation for Cotton Research and Education.

B. Technology--Process and Product Development

1. Edible Products. The use of glandless cottonseed offers promise in both food and feed uses. Feeding tests with rats and chicks showed that glandless meals produced at the Southern Division were superior to glanded meals and may approach soybean meal in nutritional quality. In addition to its importance for food products, the elimination of gossypol definitely removes the greatest barrier to broader use of cottonseed meals in poultry feeds. Glandless seed has now been processed without difficulty in two mill-scale trial runs. However, the resulting oil and meal products were not equal in quality to those produced at the Southern Division, probably because the recommended processing conditions were not closely followed. Sizable quantities of meal and flour from glandless cottonseed processed under various conditions were produced at the Southern Division to expedite research on air-classification, which may have potential for commercial production of fractions assaying 70% or more in protein content.

Continued study of process variables has resulted in many improvements in the previously reported method of using liquid cyclone separators to

produce edible cottonseed flour having low gossypol and high protein content. The process, which has now been demonstrated on a pilot-plant scale, could be carried out as part of the regular operation of existing plants for direct hexane extraction. Another phase of the research has shown that the unpleasant flavor of acetone-extracted flours might be associated with trace quantities of the reaction products of mesityl oxide, which is an impurity in acetone, with sulfhydryl compounds that are present in only small amounts in cottonseed. If this problem could be solved by inhibition, a solvent system containing acetone could also be used to extract aflatoxin in conjunction with oilseed processing. This research, directed toward the preparation of cottonseed flours and derived products for human consumption in developing countries, was supported by the Agency for International Development.

In research on the preparation of esters from cottonseed fatty acids, two methods are being investigated for their applicability to producing sucrose esters. In one process, undissolved sucrose was reacted for the first time with methyl esters of long chain fatty acids by dispersing the sucrose on the surface of an inert silica that has extensive external but practically no internal surface area. A second approach that was partially successful involved an immiscible, two-step solvent system that required relatively short reaction times, low temperatures, and only small proportions of dimethylformamide, a toxic agent. Attempts will be made to avoid the use of dimethylformamide in these processes, so that the sucrose esters produced can be used in foods.

The major components of cocoa butter-like fat made from the stearine of solvent-winterized cottonseed oil--2-elaidodipalmitin (PEP) and 2-oleodipalmitin (POF)--have been prepared and are being characterized. Melting points of PEP after various heat-treatments indicated fairly rapid conversion to the highest-melting polymorph, which is conducive to good mold release properties, whereas the conversion of POP was slower. Availability of these major triglyceride components in pure form will be useful in improving the properties of cocoa butter-like fat.

2. Fat Emulsion for Intravenous Nutrition. Research conducted cooperatively with the U. S. Army Medical Research and Nutrition Laboratory, as well as several medical schools, and supported by the Office of the Surgeon General resulted in the development of an emulsion of fractionated, pigment-free cottonseed oil stabilized with egg phosphatide. This emulsion is now being evaluated by some of the cooperators in long-term tests with animals. Although the research has now been terminated, the information should be of value for future development of similar products.

RPA 407 - NEW AND IMPROVED FEED, TEXTILE, AND INDUSTRIAL PRODUCTS FROM FIELD CROPS

A. Chemical Composition and Physical Properties

1. Improved Cottonseed Meal for Feeding to Nonruminants. Research has begun on the isolation of cottonseed protein by mechanically isolating

intact aleurone grains. In preliminary work, cottonseed was extracted with various lipid solvents, and the ultrastructure of the resultant meal observed after it was fixed with buffered osmium tetroxide, embedded in Maraglas, and thin-sectioned. Cytoplasm of tissues defatted with the acetone-hexane-water azeotrope (AHW) or with chloroform-methanol appeared swollen; with hexane, normal; and with acetone, shrunken. When fixation was eliminated to avoid hydration of the tissue, the monomeric embedding medium did not penetrate the tissue or polymerize. When tissues defatted with AHW or chloroform-methanol were embedded in methacrylate instead of Maraglas, the cytoplasm appeared normal. By providing a description of some of the physical effects of lipid solvent treatment on cottonseed meal, these studies may aid in selection of liquid vehicles for the physical isolation of proteinaceous particles after extraction.

Three additional compounds--palmitoyl chloride, methyl stearate, and methyl caprate--were reacted with gossypol in contract research at Savannah State College in Georgia. Attempts are now being made to identify the reaction products. Interesterification of gossypol with methyl esters of long-chain fatty acids seems to lead to polymerization products, but similar reactions with acids of different chain lengths will be conducted to determine the chain length required to produce products that are insoluble in alkali.

In related research, sodium gossypolate was used as an anion source in the preparation of solid complexes with a number of bivalent metals. The physical and chemical properties of the metal-gossypol complexes were determined. Infrared data revealed that the interaction of the metal ions involves a hydroxyl group and a carbonyl group of gossypol; this observation was corroborated by electronic absorption spectra. When gossypolimino derivatives were used to prepare copper complexes, the hydroxyl group of the gossypol in bis(o-carboxylphenylimino) gossypol copper (II) complex was not ionized; however, the carboxylic group was ionized, and coordination to the copper (II) occurred through the COO^- and N- of the imino group. After the properties of the various complexes are understood, a specific complex can be selected for use in the inactivation of gossypol, the effectiveness of which will then be evaluated by animal feeding tests.

Chemical examination of the seeds of 25 species of Gossypium revealed that one of the parents of American Upland cotton is evidently arboreum or herbaceum, whereas the other is gossypoides. During an investigation of the physiological effect of cyclopropene fatty acids on small animals that had ingested cottonseed products, it became apparent that the reaction of hydrogen bromide with the cyclopropene ring is not suitable for quantitative analyses. Oxidation with silver nitrate seems more promising since it is stoichiometric and is of the second order with respect to silver and of the first with respect to the cyclopropene ring. Related research has shown that the major error encountered in use of the automatic amino acid analyzer is associated with variations in the intensity of color produced when the amino acids react with ninhydrin.

In a P. L. 480 project at the University of Madras, India, the properties of the solvent system hexane-acetone-water are being investigated to obtain fundamental information needed in the design of solvent recovery systems to be used in an improved mixed solvent process for conversion of cottonseed to oil and meal. Vapor-liquid equilibrium data were obtained for the binary system acetone-water. These data were compared with values reported in the literature to verify the performance of the distillation unit to be employed in the research. The data were also used to predict heats of mixing, or enthalpy-composition figures, at one atmosphere of pressure and temperatures ranging from 0°C to the superheated region. Similar studies are being directed toward the immiscible binary system hexane-water and the miscible binary system hexane-acetone.

2. Derivatives of Fatty Acids Potentially Useful to Industry. A study of the addition of carbenes to unsaturated fatty acid derivatives of cottonseed oil has now been completed at the Indian Institute of Science, Bangalore, India, under a P. L. 480 project. Optimum experimental conditions were determined for synthesizing carboethoxycarbene adducts of methyl oleate. Two isomeric derivatives were isolated and attempts made to characterize them. One of the isomers is a solid, whereas the other is a syrupy liquid. Attempts to prepare the dibromocarbene adduct of methyl oleate were unsuccessful.

Also nearing completion is a P. L. 480 project at the Israel Institute of Technology, Haifa, Israel. In this research, iron tricarbonyl pi-complexes of the polyunsaturated moieties of tung oil and of eleostearic acid methyl esters were prepared in good yields, purified, and characterized. The regeneration of the purified polyunsaturated components from decomposition of the complexes is a potentially useful finding. There are also preliminary indications that the iron tricarbonyl pi-complexes based on tung oil may have utility as catalysts in applications such as drying oil films.

Scientists at the Hebrew University of Jerusalem, Israel, have conducted P. L. 480 research to derive new chemicals from acrylonitrile and fatty acids of cottonseed and other oils. Several Diels-Alder reactions were carried out with methyl or ethyl trans, trans-9,11-octadecadienoate as the diene; and acrylonitrile or the Ritter reaction products of acrylonitrile and methyl oleate or methyl 13-docosenoate as the dienophile. The products were isolated and characterized, and their structures were confirmed by spectroscopic methods. When the same type of condensation reaction was conducted at lower temperatures with aluminum chloride as catalyst, the yield and purity of products were improved. The presence of traces of water greatly increased the effectiveness of the catalyst. The Ritter reaction was carried out with methyl cis-5-licosenoic acid and acrylonitrile, and the product isolated in 80% yield. A procedure was developed for cyanoethylating long-chain alcohols. 1-Docosanol was cyanoethylated in 67% yield. Some of the Diels-Alder reaction products will be evaluated as plasticizers or rubber softeners.

Other P.L. 480 research at the Hebrew University is directed toward modifying unsaturated cottonseed fatty acids by metalation reactions. Ten compounds that are possible products of the carbonation and hydrogenation of the metalation products of linoleoyl or oleoyl derivatives were prepared. Through use of these model compounds, methods were developed for analyzing the reaction products by thin-layer chromatography and mass spectrophotometry. Although these procedures were not quantitative, they do permit identification of the metalation products and estimation of their relative concentrations. In continuing studies of the metalation of linoleic acid derivatives, yields of metalated product as high as 86% were obtained with N-methyl linolamide. Metalation occurred at the 13, 9, and 11 positions in decreasing order of frequency. Work was continued to improve the procedures for metalating oleic, petroselinic, and stearolic derivatives as well as the techniques for analyzing reaction products.

The synthesis and properties of newer-type glycol monoalkyl ethers based on cottonseed oil fatty acids for the suppression of water evaporation from the surface of storage areas is being investigated under a P.L. 480 project at the National Chemical Laboratory, Poona, India. A number of additional compounds were synthesized and evaluated, including three alkoxy propanols having the formula $C_nOC_3H_6OH$ ($n = 16, 18, \text{ and } 22$); two butanols, $C_nOC_4H_8OH$ ($n = 16 \text{ and } 18$); and ethyleneoxide condensation products of cetyl, stearyl, and cetostearyl alcohols. Evaporation studies were conducted with the ethylene oxide condensation products and with mixtures of the long-chain alcohols and their alkoxy ethanol derivatives. The most effective condensation product reduced evaporation about 55%; however, stearoxy ethanol reduced it about 60%. The effects of time, wind velocity, temperature, and composition of the test mixtures were established. Physical properties of the monolayers were studied, including surface viscosity, surface potential, II-A isotherms, and spreading rate. Thermodynamic properties of the alcohols, carbitols, and lower homologues of the alkoxy ethanols were determined, and dielectric constants for the long-chain alcohols were measured.

B. Microbiology and Toxicology

1. Effects of Gossypol in Feed. The Texas Agricultural Experiment Station at College Station is conducting contract research on the digestion and metabolism of gossypol in cottonseed meal. C^{14} activity measured in terms of radioactive carbon dioxide was determined in air expired by two rats that for four consecutive days were fed formyl-labeled gossypol in a basal diet with and without iron salts. Activity was detectable after half a day, continued to rise until 24 hours after the last dose, and then dropped rapidly. With each day that the rats ingested labeled gossypol, the activity in the air increased, an indication of a cumulative effect. C^{14} activity was twice as great in air expired by the rat whose diet contained iron, and the cumulative effect on successive days of ingestion of labeled gossypol was also greater. The presence of radioactive carbon dioxide in the expired air shows that to some extent the rats were able to degrade gossypol.

Related research is being conducted at the "Mario Negri" Pharmacological Institute, Milan, Italy, in a P.L. 480 project originally designed to determine the mechanism by which L-lysine counteracts the toxicity of gossypol fed to susceptible animals. Early findings that L-lysine did not exert a protective action against gossypol focused attention on the need for other inactivating systems. More recent results showed that "free" gossypol was not eliminated in the urine of rats to which the compound was administered orally. Gossypol administered to rats in which gastric ulcer had been induced by restraint did not increase the severity of the ulcer, nor did it affect bile flow. Ingestion of gossypol did induce intestinal hypertrophy; however, ingestion of iron choline citrate, sodium hydrosulfite, or ferrous sulfate protected the intestine from the toxic effects of gossypol. Another effect of oral administration of gossypol was persistent decrease in the level of iron in the plasma and in the intestines.

2. Effects of Other Undesirable Components of Cottonseed Used in Feed.

Evaluation of different experimental diets fed to trout was completed in a P. L. 480 project at the Regional Board for the Protection, Development, and Practice of Fishing in the Valley of Aosta, Aosta, Italy. When three aflatoxin-free cottonseed meals produced by the three processes commonly used in the U. S. were incorporated into trout rations at levels of 10 or 20% for periods up to 24 months, they did not induce hepatomas in susceptible trout. However, the role of aflatoxin in the induction of liver tumors in trout was confirmed, and serial histopathological examinations suggested a possible mode of formation. The role of various products in the induction of cholangitis was investigated, and the results indicated that among cottonseed components the principal cause is cyclopropene fatty acids.

The fatty aldehydes and phospholipids extracted from cottonseed by the acetone-hexane-water (AHW) azeotrope but not by hexane were shown to reduce the amount of available lysine in cottonseed proteins. Therefore, cottonseed meal produced by extraction with AHW should contain more available lysine--and hence possess greater nutritive value--than meal produced by extraction with hexane. This recently terminated research, designed to identify cottonseed constituents that cause mortalities among swine, was conducted in cooperation with the Pharmacology Laboratory at the Western Division and the Animal Husbandry Research Division, ARS.

C. Technology -- Process and Product Development

1. New Products Suitable for Industrial Use. Twenty-nine N,N-disubstituted amides of decanoic, palmitic, stearic, and oleic acids, and twelve N-substituted amides of 10-undecanoic, palmitic, oleic, stearic, and 9(10)carboxyoctadecanoic acids were prepared and characterized. One of the shortcomings of N,N-disubstituted amide plasticizers--their susceptibility to leaching from plasticized stock when exposed to soapy water--has now been overcome by adducting the amide to hexachlorocyclopentadiene. This improvement could extend its utility in applications such as shower curtains. The adduct is also less volatile. In bench tests,

N-palmitoyl-N'-methylpiperazine methiodide looked promising as a conditioner for permanent press fabrics; it will be further evaluated in laundering tests. Of all the N,N- and N-substituted amides evaluated as antimycotic agents, N-palmitoyl- and N-oleoyl-N'-methylpiperazine hydrochlorides exhibited the highest level of activity. Aspergillus flavus was one of the organisms that they effectively inhibited. However, the quaternary methiodide of these two amides is less effective than either the hydrochloride or the unquaternized amides.

RPA 702 - PROTECT FOOD SUPPLIES FROM HARMFUL MICRO-ORGANISMS AND NATURALLY OCCURRING TOXINS

A. Microbiology and Toxicology

1. Elimination of Salmonella in Cottonseed. Research was recently initiated to develop conditions that would destroy living Salmonella during the processing of cottonseed. This work is particularly important because, on the basis of recent research developments, it appears that cottonseed meals, flours, and concentrates may soon be produced commercially for use in food for human consumption.

2. Detection, Estimation, Prevention, and Elimination of Aflatoxins. Critical examination of the SURDD method of determining aflatoxin in cottonseed products, using fluorodensitometric measurements for evaluation of method parameters, disclosed that water content of the extraction solvent, activity of the silica gel used for extract cleanup, and the meal:solvent ratio all influence the recovery of aflatoxins. Modifications resulting from this study have improved the technique, which now includes fluorodensitometric measurement of aflatoxins with essentially quantitative recovery of aflatoxins added to cottonseed hulls, meats, and meals. In repetitive analysis of a cottonseed meal, precision of the technique was ± 3 to 4% . Evaluation of the stability of aflatoxin standards has shown that storage at room temperature, either in solution or in the dry state, produced changes in ultraviolet absorptivity and fluorescence, whereas storage at 0°F did not. The crude degradation product from the ingestion of aflatoxin B_1 by Tetrahymena pyriformis has been isolated and is being accumulated for identification studies.

A fundamental investigation of the biochemical mode of action of aflatoxins and their biodegradation by plant cell systems is well underway in a P. L. 480 project at Nagoya University, Anjo, Aichi, Japan. Problems in the production and purification of aflatoxin B_1 in workable quantities have been solved. Use of dimethyl formamide permitted preparation of 0.00015 molar solutions of aflatoxin B_1 . This material at 0.000015 molar concentration inhibited increase in mitochondria formation in response to wounding (slicing) of sweetpotato tissue, which was used as a model system. Inhibitors of DNA synthesis, such as mitomycin C, yielded similar results. Aflatoxin B_1 at higher concentrations inhibited formation of the enzymes peroxidase and phenylalanine ammonia-lyase during incubation of tissue

slices. Formation of succinate oxidase and cytochrome oxidase was also inhibited, although erratic results were obtained with the latter enzyme. These results suggest that aflatoxin B₁ inhibits replication of mitochondrial DNA at low concentration, but that relatively higher concentrations are required to inhibit protein synthesis.

Because of limited availability of cottonseed meal contaminated with aflatoxin, research on inactivation with basic nitrogen compounds was conducted on peanut meal during this reporting period. However, a contaminated cottonseed meal was recently obtained; treatments developed for peanut meal will now be evaluated for their efficacy in reducing aflatoxins in cottonseed meal. Enough cottonseed meal will be treated with ammonia so that it can be evaluated biologically in cattle feeding tests.

On a pilot-plant scale, extraction with 80% isopropanol in water achieved 100% reduction of aflatoxins in 15 pounds of contaminated cottonseed meal. In laboratory experiments, 80% ethanol in water removed essentially all the aflatoxin present. The effective reduction of aflatoxins by formaldehyde in the presence of alkali has also been verified. Any of these treatments could afford a means of salvaging contaminated meals so that they could be used as feed instead of lower priced fertilizer.

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RPA 406 - NEW AND IMPROVED FOOD PRODUCTS FROM FIELD CROPS

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RPA 702 - PROTECT FOOD SUPPLIES FROM HARMFUL MICROORGANISMS
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AREA 3 - PEANUT UTILIZATION

USDA and Cooperative Program

Location of Intramural Work	Scientist Man -Years F. Y. 1968			
	Research Problem Area			
	406	601	702	Total
Louisiana (New Orleans)	:	:	:	:
Chemical Composition and	:	:	:	:
Physical Properties	:	5.1	:	5.1
Flavor	1.3	:	:	1.3
Microbiology and Toxicology	:	:	6.2	6.2
Technology--Process and Product	:	:	:	:
Development	1.0	:	:	1.0
Total	2.3	5.1	6.2	13.6

Intramural program is supplemented by extramural support representing P. L. 480 funds in 1 country representing 12,262 U. S. dollars equivalent per year.

Problems and Objectives

Despite the surplus of peanuts, their price is relatively high; the domestic crop is therefore used primarily in foods such as peanut butter, confections, bakery items, and roasted nuts. However, in recent years, much of the crop has been dried and cured artificially, with the result that peanuts and their products do not always have the same desirable flavor as peanuts cured slowly in the field. Information is therefore needed on the relation of chemical constituents of peanuts to the flavor, aroma, and other properties of the processed products. In addition, new and improved products must be developed to extend domestic and foreign markets. Basic and applied research on peanut proteins is particularly important to both markets. But to assure that peanuts will continue to be utilized in food and feed products, they must be protected from contamination by fungi and mycotoxins.

Major objectives of the research are:

1. To identify chemical sources of the characteristic peanut flavor and aroma.
2. To develop new and improved products and processes.
3. To expand domestic markets by tailoring products to meet preferences of the consumer.
4. To increase commercial exports.
5. To insure the safety and wholesomeness of peanuts and peanut products.

Progress - USDA and Cooperative Program

RPA 406 - NEW AND IMPROVED FOOD PRODUCTS FROM FIELD CROPS

A. Chemical Composition and Physical Properties

1. Chemical, Physical, and Biological Properties and Structural Factors of Seed Proteins. During the reporting period, the Seed Protein Pioneering Research Laboratory, now disbanded, made considerable progress in its study of oilseeds, including peanuts.

The investigation of the ureide-metabolizing enzymes, allantoinase and allantoicase, was extended to include not only peanuts but also the germinating castor seed. In peanuts, both enzymes were distributed in the microsomal fraction of the centrifuged homogenate of the peanut. Partial purification of the two ureide-metabolizing enzymes showed that they were associated with the protein fraction that precipitates at 40 to 65%

ammonium sulfate saturation, considered to be conarachin. In this fraction were found 71.5% of the allantoicase and 76% of the allantoinase activity. Comparison of the 40-65% fractions of resting and germinating peanuts by gel electrophoresis showed that the enzyme protein was distinct from the conarachin band.

Unlike allantoinase in soybean, mung bean, kidney bean, and peanuts, this enzyme was absent in dormant castor seeds. It appeared about the third day of germination and reached maximum activity about three days later. The allantoinase of germinating castor seeds appeared to be either membrane- or particle-bound. It might be associated either with some mitochondrial particulate matter or with particulate matter from the glyoxylate cycle enzymes.

A few years ago peanuts were reported to contain certain lectins, which are plant proteins that act as agglutinating agents; since they bind to the carbohydrate coat of certain erythrocytes, they can serve as valuable materials for typing blood. The lectin reportedly isolated from peanuts with 10% sodium chloride is a weak agglutinin that binds to an unusual carbohydrate in type Gy blood, a rare form. The Gy lectin is not stable and has not been purified. Attempts were made to purify this Gy lectin from peanuts by diethylaminoethyl-cellulose chromatography and Sephadex G-200 column chromatography. Seven fractions (heart cuts) of the purified peanut proteins were obtained, freeze-dried, and sent to a medical foundation for use in experiments on blood typing.

In a continuation of the investigations of lipid metabolism in oilseeds, the position specificity of the castor bean acid lipase was determined by use of synthetic substrates having palmitic and oleic acids in known positions of the triglyceride. Results confirmed the fact that the 2-position of triglyceride substrates is cleaved by this lipase after seven to ten minutes of reaction time. It appears that the 1- and 3-position fatty acids must be removed first, but ten to thirty minutes after the reaction was initiated, the appearance of the fatty acid from the 2-position was steady. Castor seed lipase therefore offers a means of obtaining fatty acids from fats or oils rapidly and completely.

The protein activator of the lipase was compared with some of the characterized allergens of the castor seed. Although the precipitin bands and the migration patterns on gel electrophoresis of the activator of the lipase were similar to those of allergens, use of immunochemical techniques showed that the activator is not one of the well-characterized allergens. Whereas this finding excludes the possibility of a specific biochemical role of allergens in lipid metabolism of the seed, the fact that allergens can function in lipid metabolism is an interesting finding in itself.

Distribution and changes in the proteins of the peanut before and after germination were also studied by immunochemical techniques. Fourteen antigenic constituents were detected in cotyledonary extracts of the

mature peanut. There was one principal antigen in α -arachin and two in α -conarachin. Fundamental differences between the structures of these proteins are reflected by the entirely different antigenicities of these proteins. Cryoprecipitation, a characteristic of certain seed proteins of certain species, is a property of α -arachin but not of α -conarachin. Studies of the action of trypsin and of 2 M urea on arachin led to the hypothesis that arachin is composed of antigenic subunits and that the cohesion between the subunits is mostly due to hydrogen bonds. Cotyledonary and axial tissues are quite similar in their protein composition. Immuno-electrophoretic analysis of subcellular preparations confirmed α -arachin as an aleurin--that is, a protein within the aleurone grain--and α -conarachin as a non-aleurin. α -Arachin occurred in both large and small aleurone grains; α -conarachin did not occur in any of these fractions. Upon germination, α_1 -conarachin disappeared, mainly three to nine days after germination began. Before α_1 -conarachin vanished, no change in antigenicity and electrophoretic mobility was noted. The major reserve protein, α -arachin, was metabolized in a different way. At the beginning of germination, an important shift of α -arachin towards the anode was detected. The molecules retained their original antigenicity but appeared widely heterogeneous in their electrophoretic mobilities. A series of intermediary proteins may therefore be present during this period of germination. The heterogeneity disappeared about the ninth day. The results indicate that arachin constitutes the first major source of ammonia in the new seedling and, in conjunction with the α -keto acids produced, contributes to synthesis of new amino acids and protein in the peanut. It was also shown that new antigenic proteins were synthesized in both the radicle and the cotyledon of the peanut during germination. Some of these appeared to be organ-specific, but others seemed to be identical in both organs.

A new enzyme, an acid protease, was isolated from hempseed, purified, and characterized. This enzyme was not inhibited by any of the established inhibitors of proteolytic enzymes. The hempseed protease is normally particulate-bound but was freed from the bound state and solubilized with a detergent, Triton X-100. Studies on the distribution of the protease suggested that it is located in or associated with the protein bodies of the hempseed. It appears to be the protease that degrades edestin, the reserve protein of the hempseed, upon germination of the seed to provide amino acids for synthesis of proteins in the newly emerging plant. In what may be a rare instance of a seed or plant protease acting on its own natural substrate, this protease was shown to degrade its natural substrate, edestin. Proteolysis of edestin and hemoglobin (the substrate normally used in testing activity) were compared. The pH optimum of the enzyme on the hemaglobin at 50°C was found to be 3.4; on edestin, it shifts to 4.3. This latter pH is perhaps closer to the natural conditions in the seed.

Another new enzyme isolated was the one that synthesizes eleostearic acid in the developing tung nut. This enzyme appeared in the seed between the eighth and ninth week of maturation. Several buckets of maturing tung nuts, nine weeks of age, were carefully extracted to obtain acetone powder

preparations of the crude enzyme. The crude extracts readily converted oleic and ricinoleic acid to eleostearic acid in vitro. Interestingly, the enzyme was more active on ricinoleic acid, the major fatty acid of the castor seed, which is in the same family as tung. The enzyme was not very stable, however; after it was stored for six months at -30°C , its activity decreased considerably. These experiments suggest that it should be possible to prepare the more expensive types of fatty acids and unsaturated acids from cheaper sources of material by use of enzymes prepared from developing seeds at a specific stage in their maturation.

A fluorometric method for measuring lipase activity was developed, using fatty acyl esters of 4-methylumbelliferone, the brightening agent in laundry detergents. This method has the advantage of requiring extremely small quantities of enzyme and substrate.

2. Reactions of Peanut Proteins. The effect of roasting on the biological value of the proteins in Valencia-type peanuts was evaluated in feeding tests with rats. Increased roasting temperatures decreased the availability of protein, but 100% relative humidity during roasting protected the proteins from heat damage without reducing the palatability of the roasted product. The presence of fat during roasting also protected the peanut proteins from thermal damage. Roasting experiments with carbohydrate-free peanut protein isolates, conducted at 120°C and higher, revealed that both glucose (0.2%) and sucrose (4.5%) increased the loss of the nutritive value of the proteins on heating. Results of the biological evaluation were confirmed by chemical procedures, such as tests of available lysine, protein solubility, and peptic digestion. Scientists at the University of Granada in Spain, where this research is being conducted under a P. L. 480 grant, will now extend their research to Spanish-type peanuts grown in the Southwestern U. S.

B. Flavor

1. Constituents and Factors Affecting Flavor and Aroma of Processed Products. Sparging cold-pressed oil from roasted peanuts with nitrogen produced a flavor and aroma concentrate, but a single pass did not strip all the aroma from the oil. After samples of peanut butter were stored at room temperature or in a warm cabinet for a month, their fresh flavor was significantly less than that of a refrigerated sample, but a definite off-flavor was not detected. Changes in flavor during storage were accompanied by changes in the relative proportions of volatile components, as detected by gas-liquid chromatography (GLC); these differences are indicative of chemical changes as well as possible losses associated with volatilization. However, the components separated by GLC have not yet been identified.

Argentine peanuts cured and stored under different conditions have now been evaluated in contract research at the Oklahoma Agricultural Experiment Station at Stillwater. Curing treatments had a dominant influence on

organoleptic quality, whereas storage treatments had only minor effects. Curing at high temperature (120°F) produced an off-flavor that was not evident in the raw cured peanuts but developed during roasting. This curing condition also decreased moisture content, seed weight, and germination but increased the number of sound splits. Analysis of aleurone grains and fat-free meal showed that high curing temperature also increased ninhydrin-positive material, including a twofold increase in certain amino acids that are precursors of aldehydes found in peanuts. A peptide appeared to serve as a reservoir for amino acids, whereas sucrose seemed to supply the reducing sugars that react with amino acids to produce flavor and aroma. Thus, determination of the concentration of the peptide and of sucrose may guide the processor in achieving superior properties in a particular lot of peanuts.

C. Technology--Process and Product Development

1. Improved Partially Defatted Peanuts. Factorial experiments are being conducted to determine the effects of a number of variables on the shelf-life of partially defatted peanuts. A recently developed rapid method for estimating shelf-life indicated that it was increased when the peanuts were salted after rather than before roasting. To date, standard tests have shown that partially defatted peanuts can be stored under nitrogen in cans for six months. Other studies suggested that, for practical processing, sufficient oil could be removed from whole peanuts by hydraulic pressing at temperatures as low as 40°F, though removal at higher temperature was more efficient. For equal time of immersion during expansion, water soluble losses decreased as the fat content of the defatted peanut increased.

2. Edible Products for Developing Countries. During this reporting period, cottonseed rather than peanut flours have received most of the attention in research supported by the Agency for International Development. However, peanut flours have been shipped to various investigators.

RPA 601 - EXPANSION OF FOREIGN MARKETS FOR U. S. FARM PRODUCTS

A. Chemical Composition and Physical Properties

1. Properties of Peanut Proteins. Research was recently begun to investigate the chemical, biochemical, and physicochemical properties of peanut proteins; their relationship to other components of the peanut; and the effects of various processing conditions on their properties. The findings will be evaluated to determine the relationship of all of these variables to the use of peanuts in food products.

2. Properties of Peanut Lipids. Related research, also recently initiated, is designed to be a study of the chemical and biochemical properties of peanut lipids; their relation to the major peanut proteins; changes in the oil and free fatty acid content; and formation of oxidized fatty intermediates, all of which will be evaluated for their effect on the potential food value of peanut proteins.

RPA 702 - PROTECT FOOD SUPPLIES FROM HARMFUL MICROORGANISMS
AND NATURALLY OCCURRING TOXINS

A. Microbiology and Toxicology

1. Limiting Conditions for Elaboration of Aflatoxins. The environmental conditions of relative humidity and temperature under which Aspergillus flavus elaborates aflatoxins were delineated for sterile and living unshelled peanuts and for sound mature, immature, and damaged shelled peanuts in contract research at the Alabama Agricultural Experiment Station, Auburn, Alabama. Peanuts intact in the pod had lower susceptibility to mold invasion and to aflatoxin elaboration than did shelled kernels, whose resistance to mold invasion was further reduced by physical damage and overmaturity. Although immature kernels attained higher moisture levels at a given relative humidity (RH), they did not exhibit greater susceptibility to fungal attack than did sound mature kernels. For maximum protection from attack by mold and elaboration of toxin, peanuts should be held in the shell, dried quickly to moisture of 9% or less, maintained at RH of 80% or less, and kept at a temperature of 14°C or less. After shelling, the same RH and temperature should be maintained. These results are of immediate practical use in assuring that peanut products are free of toxins.

2. Inactivation or Removal of Aflatoxin from Contaminated Peanut Kernels. Both oil and dry roasting of peanuts that had been inoculated with Aspergillus flavus reduced the levels of aflatoxin (originally 130 to 6,000 ppb) by 60 to 80%, though roasting by dry radiant heat achieved the slightly better reductions. The percentage of decrease was fairly uniform at all levels. Preliminary data indicate that the improved, objective fluorodensitometric method of estimating aflatoxins, originally developed for cottonseed products, is directly applicable to peanuts, peanut meal, and peanut butter; recovery of aflatoxins is essentially quantitative. Another phase of the research indicated that US-26 peanuts are susceptible to attack by A. flavus and to elaboration of aflatoxins, a finding different from the inherent resistance reported by other workers.

Preliminary runs of continuous filtration-extraction on a pilot-plant scale indicate that with good control it is feasible to detoxify aflatoxin-contaminated peanut meal with aqueous acetone to the extent that the meal may be used as feed. The effectiveness of 80% isopropanol in water for extracting 100% aflatoxins from peanut meal has been verified on a semi-pilot-plant batch scale, and it also appears feasible to use this solvent on a continuous basis. Preliminary experiments revealed that 80% ethanol in water is similarly effective. Cooking experiments have verified the utility of formaldehyde in the presence of alkali for reducing aflatoxin levels, and five other reagents (crotonaldehyde, formylhydrazine, isobutyronitrile, benzonitrile, and 3,5-dimethylpyrazole), also in the presence of alkali, have significantly reduced aflatoxin content in contaminated peanut meal. The organism Tetrahymena pyriformis was used to evaluate the nutritional value of contaminated peanut meals that had received detoxification treatment.

Factorial experiments designed to evaluate the effects of moisture, time, temperature, and ammonia pressure on the detoxification of peanut meals containing aflatoxin have provided information that will influence the choice of operating parameters. The recent development of densitometric techniques for objectively estimating aflatoxin content has permitted the reconciliation of inconsistencies obtained in analysis of variance of data from previous factorial experiments. Results obtained at two levels of ammonia pressure and two levels of reaction temperature were significantly different, the higher level of each variable achieving the greater reduction of aflatoxin. Two basic nitrogenous compounds--ammonium carbonate and ethylenediamine--appear to be practical reagents for lowering the aflatoxin level in contaminated peanut meals.

Treatments to inhibit the growth of mold and production of aflatoxins on peanuts were evaluated in contract research at the Oklahoma Agricultural Experiment Station in Stillwater. In the laboratory, several commercially available fungicides (Duter, Phalatan, Difolatan, Captan, and Orthocide) appeared promising. However, in field studies, no consistent relationships could be established for the occurrence or inhibition of aflatoxin as a function of the application of fungicide. Combinations of different fungicides were evidently no more effective than each one used separately at an equivalent concentration.

Publications - USDA and Cooperative Program

RPA 406 - NEW AND IMPROVED FOOD PRODUCTS FROM FIELD CROPS

Chemical Composition and Physical Properties

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RPA 702 - PROTECT FOOD SUPPLIES FROM HARMFUL MICROORGANISMS
AND NATURALLY OCCURRING TOXINS

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^{1/} Publication resulting from research under grant of P. L. 480 funds to the foreign institution.

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AREA 4 - CITRUS AND SUBTROPICAL FRUIT UTILIZATION

(RPA 403 - NEW AND IMPROVED FRUIT AND VEGETABLE PRODUCTS)

USDA and Cooperative Program

	:	Scientist	:
Location of Intramural Work	:	Man-Years F.Y. 1968	:
Florida (Winter Haven)	:		:
Flavor	:	8.6	:
	:		:
Color, Texture and Other Quality Factors	:	1.1	:
	:		:
Technology--Process and Product Development	:	4.2	:
	:		:
Texas (Weslaco)	:		:
Flavor	:	2.5	:
	:		:
Technology--Process and Product Development	:	2.2	:
	:		:
Total :	:	18.6	:

Intramural program is supplemented by extramural support representing (a) 0.8 SMY's at State Agricultural Experiment Stations^{1/}, and (b) 1.2 SMY's at other U. S. institutions^{2/}.

^{1/} All on Chemical Composition and Physical Properties.

^{2/} Chemical Composition and Physical Properties 0.6; Flavor 0.6.

Problems and Objectives

Advances in the citrus and subtropical fruit industry are needed to utilize the already large but increasing production of these fruits to the economic advantage of growers, processors, and consumers. Research should be conducted not only to relate chemical components of citrus to its natural flavor and color but also to solve problems caused by bitterness and other off-flavors in grapefruit and oranges. New products should be developed to use more fruit, to attract consumers, and to reduce shipping costs; a particularly important aspect is utilization of a larger proportion of the fruit for food, as in comminuted whole citrus products. Processing procedures and equipment must also be improved. In addition, rapid, sensitive, and economical tests of quality must be devised to assure that the most desirable qualities of citrus and subtropical fruit are conveyed to the consumer.

Important goals of the research are:

1. To develop new and improved products from citrus and avocado.
2. To use more of the whole citrus fruit for food purposes.
3. To identify the sources of undesirable flavors in citrus and to develop methods to prevent them.
4. To expand markets by tailoring products to meet the needs and preferences of consumers.
5. To improve processing methods to preserve or enhance the natural flavor, color, and other desirable properties of citrus products.

Progress - USDA and Cooperative Program

A. Chemical Composition and Physical Properties

1. Relation of Ribonucleotides to Consumer Acceptability of Processed Products. A grant was recently awarded to the Florida Agricultural Experiment Station at Gainesville to investigate the role of ribonucleotides in consumer acceptability of processed citrus products and as an index of quality. Attempts will also be made to determine the potential of these compounds for controlling changes in the fruit that affect processed products.

2. Estimation of Peel Solids. Scientists at the Stanford Research Institute, South Pasadena, California, are conducting contract research to develop an organic acid index to assess the amount of peel solids in orange and grapefruit paste, puree, and juice. Satisfactory methods were developed for separating oranges and grapefruit into segment juice, rag, peel juice,

and pressed peel. Techniques were also devised for separating the organic acids in each fraction into free acids and combined acids and for quantitatively separating and analyzing the individual acids. These studies showed that free oxalic acid evidently is not a normal component of the segment or peel juice of either oranges or grapefruit. Since combined oxalic acid is the major acid of pressed orange peel, an "oxalate index" may provide an indication of peel solids present in orange juice. However, this technique would not be applicable to grapefruit, since combined oxalic acid is not a component of either juice or peel.

B. Flavor

1. Improved Flavor and Quality of Citrus Products. Enzyme reactions are being studied to determine their role in the development of flavor in citrus; eventually, such systems may be used to enhance flavor. In recent research, juice from mature oranges and grapefruit was shown to differ quantitatively from juice of green immature fruit in the ratio of reduced to oxidized forms of nicotinamide adenine dinucleotide (NADH/NAD). The higher the Brix/acid ratio, the higher the ratio of NADH/NAD. This correlation suggests that compounds known to affect the reduction/oxidation ratio should be investigated as possible regulatory agents of acidity in fruit on and off the tree. Mature citrus fruit has also been shown to have enzymes characteristic for metabolic reactions involving glucose, citric and malic acids, and ethanol and for the synthesis of aliphatic compounds. Although orange juice contains enzymes capable of synthesizing the β -hydroxybutyryl moiety from acetate through acetoacetyl coenzyme A, enzyme preparations from orange would not synthesize the β -hydroxymethylglutaryl moiety (BHMg) from acetoacetyl coenzyme A or from mevalonic acid from BHMg-coenzyme A. Therefore, if mevalonate is the precursor of terpenoids in the orange, it arises by reactions either outside the fruit or unique to it.

In research on the composition of essential citrus oils, six more compounds were synthesized as part of the effort to complete the collection of the 200 known components of citrus oil; 164 are now available. This collection will be useful in evaluating the contribution of individual compounds to flavor as well as providing known samples for comparison with unknown components isolated from various citrus oils. Also continuing is the analysis of the composition of aroma oil, a byproduct of the recovery of essence from orange juice and a valued flavoring additive. In an analysis of the carbonyl fraction of Valencia orange peel oil, now completed, most of the compounds isolated were aldehydes, ketones, and esters. The major compounds responsible for the unpleasant odor of stripper oil, also a byproduct, have been identified, and a method for their removal devised. Use of stripper oil in mechanics' hand cleaner is an example of an end use that would benefit if the odor of the oil were improved.

2. Prevention of Deterioration of Flavor. Sufficient quantities of four of the five known neutral flavones needed for taste evaluation are now available; the exception is sinensetin, which is being accumulated by both

isolation and synthesis. The identity of one of the unknown compounds in the neutral fraction is also being investigated. Although the principal UV maxima of this unknown is very close to that of 5,7,3',4'-tetramethoxyflavone, a comparison by thin-layer chromatography showed that it is not identical to the latter synthesized compound. Synthesis of auranetin, the 3,6,7,8,4'-pentamethoxyflavone isolated elsewhere from kamala orange peel, is being attempted.

In orange and grapefruit concentrates stored for thirteen months, hydrolysis of juice lipids to their respective fatty acid moieties occurred even at 0° F and was accelerated at 85° F; these reactions may account for changes in flavor during storage. Various citrus species, all of which have their own characteristic fatty acid composition, are being studied to determine if some species--for example, tangerine--are particularly susceptible to lipid oxidation. Fatty acid composition of seed lipids does not appreciably differ from species to species; nor is there much seasonal variation. However, the finding that the fatty acid composition of seed lipids is very different from that of the respective juice lipids indicates that crushed seeds do not extensively contribute lipids to the juice during processing. Since natural and added peroxides could not be detected in lipid extracts from stored citrus concentrates, these lipid oxidation intermediates appear to be unstable in citrus media. In another phase of the research, highly colored extracts from orange peel raised the color-grade of poorly-colored juice at concentrations as low as one drop to 30 ml.

In contract research at Ohio State University Research Foundation, Columbus, Ohio, a number of variables are being studied for their effect on browning of sugar-amino mixtures in aqueous solutions. Factors investigated include molar ratio of amino acid to sugar; water content; pH; and presence of various organic components, such as acids, sugars, and amino acid. Prevention of browning reactions would help extend the storage life of citrus products such as orange juice crystals.

3. Bitter Constituents and Related Components of Grapefruit. A major achievement in recently terminated research on bitterness in grapefruit products was development of a new method for the biosynthesis of radioactive naringin and its tasteless isomer, naringenin-7 β rutinoside. In a related project, the six major flavanone rhamnoglucosides in grapefruit--three of which are bitter and the other three, their tasteless isomers--were determined quantitatively in fruit harvested at monthly intervals. Since the maximum formation of the bitter flavone naringin is confined to a relatively brief period early in the season, cultural practices, such as setting the fruit later, may help improve its flavor. Synthesis of lycopene and carotene in the flesh of Redblush grapefruit and synthesis of carotenoids in the flesh of Ruby blood oranges were influenced by temperature, whereas formation of anthocyanin in blood oranges was affected by both temperature and maturity. Evaluation of climatic factors may lead to more accurate methods of predicting the time that fruit reaches maturity and optimum quality for processing.

C. Color, Texture, and Other Quality Factors

1. Extracts from Peel to Enhance Color. Finely ground peel of early and mid-season varieties of oranges was extracted with normal hexane to yield highly-colored pigments that appear to be useful in improving the color of juice. Treatment of the colored extracts with alcoholic sodium hydroxide darkened their color and removed brown and green pigments; this result may indicate that chemical changes are occurring.

D. Technology--Process and Product Development

1. Enzymatic Debitting of Grapefruit Products. Debitting grapefruit sections and juice by the use of naringinase at relatively low levels was attempted in contract research conducted by the Florida Agricultural Experiment Station at Lake Alfred. Since Florida grapefruit contained little bitterness during the 1967-68 season, it was necessary to test off-bloom fruit. A workable system was devised for adding naringinase to jars of hand-sectioned grapefruit. The pack of sections produced will be evaluated by taste tests to determine the value of enzymatic debittering. Different finisher pressures used during the processing of grapefruit juice did not cause a significant difference in naringin levels. Analyses of juice to which naringinase had been added before it was canned showed that pasteurization had completely inactivated the enzyme so that it was unable to decrease bitterness in the juice during storage.

2. New and Improved Products from Citrus and Subtropical Fruit. To utilize a larger proportion of whole fruit, research has begun on the preparation of various products from comminuted citrus. Preliminary work concerned the utilization of water-soluble extracts from the peel of grapefruit and oranges. Concentrates of the extracts contained a substantial quantity of sugar. Acid hydrolysis only slightly reduced the bitterness of the grapefruit extracts. Grapefruit peel steeped in hot water, dried at 105° C, and then ground into a coarse flour did not taste bitter but did retain a slight citrus flavor and aroma. Samples of comminuted whole grapefruit and oranges, as well as their peel, pulp, and rag, have been frozen to provide a source of material during the summer months, when citrus is unavailable.

Foam-mat dried products also offer promise of increased consumption of citrus. In research conducted in cooperation with the Florida Citrus Commission and the Western Utilization Research and Development Division, laboratory procedures were developed to permit flavoring additives for foam-mat dried citrus crystals to be encapsulated in molten sugar, as done commercially. This technique makes it possible to compare different additives that are available only in small quantities. Another new system has been developed for converting orange essence to an anhydrous form so that it can be used in the crystals. When this dry essence and commercial "locked-in" peel oil were incorporated into orange crystals, samples of instant juice tasted more like fresh fruit. The use of higher oil levels, acceptable to untrained tasters, has considerably increased storage life

of the crystals. But there has been improvement not only in the product but also in the process: the combination of densifying, grinding, and sieving after dehydration into a continuous system has increased its attractiveness to industry.

Another approach to developing new and improved products is the use of freeze-drying. Samples of sugar-water solutions, orange juice, and grapefruit juice having concentrations of solids ranging from 10 to 60% were frozen, ground to different particle sizes, and then freeze-dried under standard conditions. Moisture was removed more easily and completely from samples having smaller particle size. This effect on drying rates was more pronounced when the concentration of solids was high. Thus, high-Brix solutions, in which the dried layer provides a limiting factor for moisture removal, would be easier to freeze-dry if they were ground to finer particle size. Freeze-drying has potential for providing additives to enhance the flavor of citrus products--for example, the flavor of foam-mat dried orange powder was improved by the addition of freeze-dried orange juice containing orange essence.

In addition to research on freeze-dried citrus, a freeze-dried avocado salad product was prepared and retained acceptable flavor when it was stored under nitrogen or in vacuum for 48 weeks at 40° F or below, 16 weeks at 68° F, and 3 weeks at 100° F. Its color was stable--that is, there was no loss of carotene--at all storage temperatures for 48 weeks when air was excluded. The carotenes are among the most labile components of the system. Since the carotene content in air packs decreased far more rapidly than did unsaturated acids, preferential oxidation of the carotenes may have a sparing effect on the autoxidation of the unsaturated fatty acids. Control of the oxidation and/or autoxidation of the unsaturated acids may be a better approach to stabilizing the flavor and odor of certain dehydrated foods than is prevention of oxidation of β -carotene per se.

Publications - USDA and Cooperative Program

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AREA 5 - VEGETABLE UTILIZATION

(RPA 403 - NEW AND IMPROVED FRUIT AND VEGETABLE PRODUCTS)

USDA and Cooperative Program

	:	Scientist	:
Location of Intramural Work	:	Man-Years F.Y. 1968	:
Florida (Winter Haven)	:		:
Technology--Process and Product Development	:	1.1	:
Louisiana (New Orleans)	:		:
Technology--Process and Product Development	:	1.2	:
North Carolina (Raleigh)	:		:
Technology--Process and Product Development	:	5.2	:
Texas (Weslaco)	:		:
Technology--Process and Product Development	:	2.7	:
Total	:	10.2	:

Problems and Objectives

The market for fresh vegetables has suffered from the effects of rapid spoilage, seasonal surpluses, and increasing demand for convenience foods. Stable, attractive, and convenient processed vegetable products must therefore be developed. However, much research is needed to solve problems incurred in the processing. For example, although most of the cucumber crop is brine-cured, spoilage during curing frequently causes high losses. To increase the utilization of dehydrated sweetpotatoes, their shelf-life should be extended and new products developed to combine the flakes with other foods. Celery, already an important flavoring ingredient, could become much more widely used if factors responsible for variations in the intensity of flavor could be controlled during processing and if more convenient products were developed. To improve processed vegetables, there is also need to determine the effect of climate, soil, cultural practices, and variety upon the raw material, particularly for vegetables like tomatoes, in which color, flavor, and texture are frequently poorer when they are grown in warm instead of temperate regions.

More specific objectives of the research are:

1. To identify the effect of different characteristics of raw vegetables on quality of the processed products.
2. To improve processes for fermented vegetables, particularly cucumbers.
3. To modify and enrich products from sweetpotato puree and flakes.
4. To develop products having improved natural celery flavor.
5. To develop new and improved products from other southern-grown vegetables, such as tomatoes and carrots.

Progress - USDA and Cooperative Program

A. Chemical Composition and Physical Properties

1. Purification of Inhibitor of Enzyme That Softens Cucumbers. In the final stages of a grant to the Research Triangle Institute, Durham, North Carolina, the crude pectinase inhibitor extracted from the leaves of sericea and previously identified as a polymeric pro-anthocyanidin based on delphinidin was purified almost fourfold, as measured by inhibition of activity of the enzyme. This natural inhibitor prevents enzymatic softening of fermenting cucumbers, and it may serve the same function for brined cherries. Another potential use is as a viricide for such organisms as the tobacco mosaic virus.

B. Technology--Process and Product Development

1. Fermented Cucumber and Other Vegetable Products. In fourteen varieties of cucumbers, differences existed in total carbonyl content as well as in the ratio of saturated to unsaturated carbonyl compounds. Although the total carbonyl content was lower in fruits with large diameter, a higher proportion of these carbonyls consisted of the unsaturated type. A combined physical-chemical sanitizing treatment was devised as a replacement for heat-shocking in the fermentation of cucumbers; anticipated benefits include lower cost of equipment and treatment and higher rate of processing bulk cucumbers. In related research on the autoxidation of carotenes, radioactive β -carotene added to precooked dehydrated sweetpotato flakes stored in an oxidizing atmosphere behaved the same as native carotenes. The end products of carotene oxidation in the flakes appeared to be low molecular weight fragments, including carbonyls, and polymers. Since carotenes are obviously involved in lipid oxidation and the development of off-flavor, their role must be defined before optimum storage conditions can be selected for processed foods. Various phases of the research are conducted in cooperation with the Pickle Packers International, Inc., and the North Carolina and Michigan Agricultural Experiment Stations.

2. New and Improved Dehydrated Sweetpotato Products and Processes. In the processing of Goldrush sweetpotatoes to make precooked flakes by the enzyme activation method, heating is a critical step, affecting gelatinization of starch and influencing the α -amylolytic action that controls the conversion of starch. The conditions required for cured potatoes, in which the enzyme concentration is high, differ from those optimal for freshly harvested roots, in which amylolytic activity is limited. The remarkable constancy of glucose and sucrose during all processing steps, despite wide variance in the raw roots, suggests two types of amylolysis: one functioning during storage to effect changes in sucrose and glucose, the other during heating to produce maltose alone. Other experiments showed that larger screen size used in a hammer mill improved the quality of flakes from uncured sweetpotatoes. Although samples of drum-dried sweetpotato pie mix packed in nitrogen were rated slightly better than those packed in air, the latter were judged fair to good after storage for thirteen months.

3. More Flavorful Dehydrated Celery Products. A faster and more efficient procedure for obtaining high quality celery essential oil in good yield from celery waste is being developed by use of a recently acquired laboratory evaporator. Research toward identification of major carbonyl compounds in celery oil is continuing. Microsaponification and esterification procedures were perfected to permit the total reaction mixture to be examined by gas chromatography. By these techniques, three esters were identified, and six other esters were tentatively identified. A carbonyl compound whose odor resembles that of apples was isolated from celery oil, and attempts are being made to synthesize it. These studies of the chemical composition of celery essential oil suggest that it is highly complex and that the flavor profile of fresh celery cannot be attributed to only a few compounds.

4. Improved Tomato and Other Vegetable Products. In cooperation with the Texas Agricultural Experiment Station, Crops Research, and industry, innovations in food technology are being applied to the development of improved products from southern vegetables. In experiments conducted during 1967, Chico variety tomatoes peeled in a hot calcium chloride solution picked up much more calcium than did tomatoes tested in 1965 and 1966. Many variables, such as growing conditions, variety, and maturity, evidently affect the toughness of tomato skin, which in turn causes variability in the time required to split the skins in the calcium solution and thus in the desired firming effect. Other research was directed to finding a substitute for citric acid, which is now used in canned salad pack tomatoes but causes a harsh, biting taste. However, the four acids tested--maleic, fumaric, lactic, and d-tartaric--did not improve the flavor. Recently initiated work concerns the processing characteristics of tomatoes, with emphasis on pectin and its quality. Molecular sieve fractionation columns have been set up, and preliminary experiments are being conducted on flow rates, pressure heads, and separations. Tomatoes of known background and commercial quality have been planted. In still another phase of the work, extreme ranges in the concentration of total carotenoid pigments were found among twenty-four varieties of carrots analyzed for carotenes and xanthophylls.

Publications - USDA and Cooperative Program

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AREA 6 - NAVAL STORES UTILIZATION

(RPA 401 - NEW AND IMPROVED FOREST PRODUCTS)

USDA and Cooperative Program

	:	Scientist	:
Location of Intramural Work	:	Man-Years F.Y. 1968	:
Florida (Oluſtee)	:		:
Chemical Composition, Physical	:		:
Properties and Structure	:	0.2	:
	:		:
Technology--Process and Product	:		:
Development	:	13.8	:
Total:		14.0	:

Intramural program is supplemented by extramural support representing 3.2 SMY's per year at U. S. institutions other than State Agricultural Experiment Stations^{1/}.

1/ All on Technology--Process and Product Development.

Problems and Objectives

Naval stores are unusual agricultural products in that they are used almost exclusively as chemical raw materials. Although rosin, turpentine, and pine gum consist of organic compounds with unique chemical structures that are difficult to duplicate synthetically, these naval stores products face increasing competition for markets from products derived from petroleum and coal tar. Research is needed to retain or expand industrial markets for naval stores, particularly in large-volume outlets such as polymers, plastics, elastomers, resins, plasticizers, surface coatings, adhesives, textile finishes, odorants, and agricultural chemicals. Although about one-third of the rosin produced in this country is already exported, research to convert rosin to more expensive derivatives would not only increase the value and the amount of rosin exported but also benefit domestic markets.

Major objectives of the research are to develop:

1. Basic knowledge of the composition and properties of pine gum, rosin, turpentine, and their derivatives.
2. New and improved chemical intermediates from rosin, resin acids, terpenes, and pine gum.
3. New and improved industrial products--particularly polymers such as polyurethanes, polyesters, and polyamides--from rosin, turpentine, and pine gum.

Progress - USDA and Cooperative Program

A. Chemical Composition, Physical Properties and Structure

1. Composition and Properties of Pine Gum, Rosin, Turpentine, and Derivatives. Evaluation of stump wood of ponderosa pine indicated that this wood would probably not be suitable as a source of naval stores products unless given special processing. Rosins obtained from extracts of the wood have lower acid numbers and softening points than do commercial wood rosins. These undesirable properties appear to be due to unidentified neutral materials that are not found in commercial rosins. In addition, the turpentine is very different from turpentine recovered from longleaf pine stumps. Also, the pine oil contains about 55% longifolene, whereas commercial pine oils contain 60 to 70% α -terpineol. In another phase of work, an improved method was developed for the separation of maleopimaric acid and fumaropimaric acid from maleic- and fumaric-modified rosin. Fumaropimaric acid, evaluated by the Walter Reed Army Institute of Research, was very effective in preventing guinea pigs from rejecting grafts of skin from another guinea pig and was less toxic than most materials tested. It also acted as an antihistamine and an anticoagulant.

Research was continued under a P. L. 480 grant at the Juan de la Cierva School of Technical Investigations, Barcelona, Spain, to develop new or improved methods for synthesizing, isolating, and purifying selected terpene alcohols for use as standards in instrumental methods for determining the composition and properties of products made from pine gum. In recent work, five new terpene alcohols and several additional intermediates were synthesized. Techniques for the preparation and purification of pure samples of new p-menthanols, p-menthenols and p-menthadienols were developed. Care was taken to avoid contamination by positional or stereochemical isomers. Infrared and nuclear magnetic resonance spectra of 61 terpene derivatives were obtained. The ultraviolet spectra of those compounds having characteristic absorption in this region were also obtained. This basic information will aid in developing new industrial uses for naval stores products.

B. Technology--Process and Product Development

1. Chemical Intermediates from Rosin, Resin Acids, Terpenes, and Pine Gum. Poor yields were obtained in most of the screening experiments to produce useful chemicals from terpenes and resin acids by free radical addition of functional groups; this result strongly suggests that hydrogen abstraction from both terpenes and resin acids competes with the desired addition to the double bond. It appears that free radicals from the initiators and from the intended addend can do this. Steric factors involving both the addend and the pine gum component also seem to affect the course of the reaction. Since the availability of labile hydrogen and the general bulk of the molecules are fundamental properties of the terpenes and resin acids, it is unlikely that further process development would solve the problem of low yields. Only in the case of beta-pinene were technologically practical additions obtained with any variety of compounds. Only the dialkyl phosphite showed any real promise for increasing the utility of other terpenes. However, this delineation of the scope of the reaction will facilitate future selection of reactions to be tested for increasing the utility of pine gum in specific end uses.

Studies have shown that it is possible to get selective addition to one of the double bonds of abietic acid photochemically. The yield of adduct was improved by using the methyl ester of abietic acid instead of the free acid itself to add methanol under the influence of ultraviolet light. The structure of the major product has been established, and progress has been made toward isolating and identifying some of the minor products. Products obtained by radiating abietic acid or its methyl ester in pentane and in ethanol are also being investigated. The preliminary results with ethanol suggest that the wavelength of the activating light may affect the course of the reaction.

The preparation of resin acid dimers from gum rosin is being investigated in contract research recently initiated at Battelle Memorial Institute, Columbus, Ohio. Products of this type should provide new outlets for rosin.

Contract research recently completed at the University of Florida has demonstrated that the products obtained from the dimerization of alpha-pinene with different catalysts are not all alike and has therefore provided a logical basis for selecting conditions to yield products for specific uses. Several processes were developed for converting alpha-pinene to dimers in good yields. They appear practical from the technological standpoint, but economic practicality will of course depend on the value of the products as well as cost of alpha-pinene. Results of the efforts to convert the dimers to useful reactive derivatives were less successful than hoped for. For example, ozonolysis gave mixtures of acids and neutral products from some of the dimer mixtures and little or no reaction with others. A crystalline diepoxide was obtained in good yield from one of the dimers produced with phosphoric acid catalyst. A well-characterized maleic anhydride adduct was obtained from the dimer produced with a zinc chloride-nitromethane catalyst system.

Rapid procedures based on the use of singlet oxygen have been developed for the peroxidation of pine gum and gum rosin. The products have peroxide contents in the range obtained via photosensitized oxidation. The reactivity of photosensitized-oxidized pine gum and levopimaric acid transannular peroxide with various reagents and under various conditions indicates that these two materials are potentially useful as chemical intermediates. The various peroxidized products have shown utility in the polymerization of vinyl monomers. Large samples of photosensitized-oxidized pine gum and the transannular peroxide have been prepared for future evaluation as vulcanizing agents for silicone rubber, ethylene-propylene rubber, and carbon-black filled polyethylene. Sizable samples of the following derivatives have also been prepared: hydrogenated pine gum and hydrogenated maleic- and fumaric-modified pine gum, for evaluation in adhesives; the monoacid chloride of maleopimaric acid, for evaluation in heat-resistant polyimide-amide polymers. Rapid processing of pine gum at 150°C instead of at the conventional temperature of 165°C has been found to give a rosin that contains as high as 17% levopimaric acid.

The behavior of the four conjugated dienic resin acids--levopimaric, abietic, neoabietic, and palustric--and their methyl esters at 200°C in the presence and absence of added basic and acid catalysts has been elucidated for the first time. Isomerization and disproportionation seem to be acid-catalyzed reactions. Methyl levopimarate in the presence of base at high temperature gave a mixture of several new and unusual compounds in good yield. Both levopimaric acid and gum rosin were decarboxylated with catalysts such as phosphoric acid to give a conjugated dienic hydrocarbon, which was reacted with fumaric acid to produce a new dicarboxylic acid potentially useful in the modification of unsaturated polyester-styrenated laminating resins. When gum rosin was distilled, the distillate was a rosin of excellent color, and the pot residue (20-35%) was a monobasic product that may prove useful in adhesives and other applications.

Practical processes have been developed for the preparation of polyglycols from rosin, resin acids, and pine gum. Contrary to previously reported research results, the acid-catalyzed reactions of formaldehyde and resin acids and the oxonation of rosin acids can be used for the introduction of hydroxymethyl groups into resins in good yields. Conversion of the acid functional groups to hydroxymethyl groups via reduction resulted in poly-substituted derivatives, which were further reacted with propylene oxide to yield polypropylene glycol ethers. In addition, hydroxymethyl-substituted resin acids and polybasic acids formed by the Diels-Alder reaction of rosin with acrylic and fumaric acids gave useful polyglycol esters when reacted with propylene oxide.

Research is in progress to develop diamines and diisocyanates from gum rosin and its derivatives for use in making polyurethane polymers. Several intermediates for the preparation of the desired diamines and diisocyanates have been synthesized and characterized. Simple methods have been developed for converting a hydroxymethyl substituted resin acid to an aminomethyl derivative and for converting the carboxyl group to cyanomethyl and aminomethyl groups. Initially, the tosylate ester of 12-hydroxymethyldihydroabietonitrile will be converted to the dinitrile and thence to the diamine and the diisocyanate. This route to the diamine, though less direct than that originally planned, overcomes difficulties previously encountered with compounds having a hydroxymethyl group in the C_4 position; heating the tosylate ester of such compounds resulted in an elimination reaction rather than the desired substitution.

2. Industrial Products from Rosin, Turpentine, and Pine Gum. Research is being conducted on the preparation and evaluation of polyurethanes from polyols derived from rosin, resin acids, and pine gum. When the methyl ester of gum rosin rather than gum rosin itself was oxonated, not only was the yield of reaction products 30% better but they were also more easily separated. Nearly pure methyl tetrahydroabietate, methyl monohydroxymethyltetrahydroabietate, and methyl dihydroxymethyltetrahydroabietate were isolated. Water-white, crystalline diols and triols produced from these compounds will be evaluated in polymers. Products similar in composition to those produced by the oxonation of rosin have been obtained from the reaction of abietic acid, formaldehyde, and acetic acid. If the techniques used on oxonated rosin can be applied to formaldehyde-modified rosin, the resulting process will be less costly than oxonation. Tough, stiff, strong polymers have been obtained by incorporating the rosin derivatives 12-hydroxymethyldihydroabietic acid and 12-hydroxymethylabietol into certain commercial polyurethanes.

In evaluations of selected naval stores derivatives as pressure sensitive adhesives and rubber tackifiers, the contractor (Battelle Memorial Institute) found that the best product was the polyester prepared from diethylene glycol, rosin modified with acrylic acid, and maleic anhydride. The second best product was a similar polyester in which fumaric acid was substituted

for the maleic anhydride. Of all compounds tested, these two materials also showed the best aging characteristics. Other naval stores derivatives, including pine gum modified with maleic anhydride or fumaric acid, the mono- and diesters of rosin, and the alpha olefin epoxides, also appear promising, particularly as rubber tackifiers.

Pine gum and gum rosin derivatives will be evaluated as additives for concrete in contract research recently initiated at Battelle Memorial Institute. Since certain chemical additives have been found to improve the properties of concrete and thus to increase its versatility, such applications may open new markets for naval stores products.

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^{1/} Publication resulting from research under grant of P. L. 480 funds to the foreign institution.

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AREA 7 - SWEET SORGHUM UTILIZATION

(RPA 406 - NEW AND IMPROVED FOOD PRODUCTS FROM FIELD CROPS)

USDA and Cooperative Program

	:	Scientist	:
Location of Intramural Work	:	Man-Years F.Y. 1968	:
Texas (Weslaco)	:		:
Chemical Composition and Physical	:		:
Properties	:	1.2	:
Total:	:	1.2	:

Problems and Objectives

The Lower Rio Grande Valley, which is largely dependent on an agricultural economy, must have a greater selection of crops for diversification to meet unfavorable environmental and marketing conditions that frequently beset the area. One of the crops that has potential for providing profitable diversification is sweet sorghum, particularly since new disease-resistant varieties with high sugar content are now available. The modest water requirements of sorghum and the subtropical climatic conditions conducive to an extended growing season also increase its attractiveness. In addition, integration of processing of sorghum with that of beet and sugarcane would extend the use of costly installations in sugar factories. However, to achieve these goals, research is needed to develop practical methods for the recovery of sugar from sweet sorghum.

More specific objectives of the research are:

1. To explore chemical and physical procedures for removing nonsugars from sweet sorghum juices.
2. To develop an economical process to recover the sugar from sweet sorghum.
3. To evaluate the processing characteristics of newer sorghum breeding lines grown under different agricultural practices.

Progress - USDA and Cooperative Program

A. Chemical Composition and Physical Properties

1. Recovery of Sugar from Sweet Sorghum. All field materials from the 1967 harvests in the Weslaco and San Antonio-Winter Garden areas have been analyzed. Varieties having good yield of stalks per acre and of sugar per ton of stalks were selected for further study. Field studies also indicated that periods of heavy borer infestation are seasonal and will therefore justify more extensive control experiments. When juice clarification was followed by treatment of the dilute syrup to prevent enzymatic or other deterioration of its sugars, the starch content was reduced to insignificant levels and juice purity was further increased. Laboratory studies revealed that difficulties in juice clarification resulted chiefly from insufficient phosphate content, a situation easily resolved by the addition of phosphoric acid or calcium superphosphate. This research is conducted in cooperation with the Texas Agricultural Experiment Station and Crops Research.

Publications - USDA and Cooperative Program

None.

AREA 8 - RICE UTILIZATION

(RPA 406 - NEW AND IMPROVED FOOD PRODUCTS FROM FIELD CORPS)

USDA and Cooperative Program

	:	Scientist	:
Location of Intramural Work	:	Man-Years F.Y. 1968	:
Louisiana (New Orleans)	:		:
Chemical Composition and Physical	:		:
Properties	:	3.2	:
Total	:	3.2	:

Intramural program is supplemented by extramural support representing P. L. 480 funds in 1 country representing 7,394 U. S. dollars equivalent per year.

Problems and Objectives

In the United States, the capacity for producing rice has increased faster than domestic consumption and exports. Detailed knowledge of chemical composition and physical properties of rices is needed to guide milling, processing, and product development. New and diverse food products that are economical to manufacture, convenient to prepare, and attractive in flavor and texture must be developed to increase the consumption of rice both domestically and abroad. Research is also needed to develop new and practical procedures for preventing or sealing checks and altering plasticity of rice kernels to improve milling yields.

Current objectives of this research are:

1. To identify the characteristics of the untreated or treated, whole or fractionated kernel that may be used to predict potential commercial uses.
2. To develop new and improved rice products from the flour and residual kernels prepared by deep-milling.

Progress - USDA and Cooperative Program

A. Chemical Composition and Physical Properties

1. Distribution of the Proteins. Intact protein bodies were isolated from rice endosperm at neutral pH and low temperature by differential centrifugation. These protein bodies readily broke down at lower pH or higher pH and high temperature. Integrity of protein bodies was maintained best with 0.5 molar sucrose in 0.1 molar phosphate buffer at pH 7.2 and 0°C. Electron microscopic examination of these organelles showed a distinct membrane at the peripheral boundary. The lamellar structure within, which was similar to the annual rings observed in growing trees, surrounded a very dense region in the center of the protein bodies. This research is being conducted under a P. L. 480 grant to Kyoto University, Kyoto, Japan.

2. Composition and Properties of Rice Flours and Other Products. Research is continuing on the chemical composition of high-protein rice flours prepared from six varieties of commercially milled rice and two varieties of solvent milled rice. The Satake Rice Whitener, a commercial huller, was successfully used to produce high-protein rice flour. Interrelationships between the nature of the milled rice and the depth of material removed affected the characteristics of the flour. Since a high proportion of chits was produced, the equipment should be modified. Although the protein content of the flour was enhanced by air-classification, the process was not efficient. In another phase of the work, tasty rice chips that have the appearance of potato chips were prepared from white rice;

preliminary tests indicate that they will store safely for three months under air in glass containers. Storage stability tests are also being conducted on a ground, extruded brown rice product, which did not become rancid at room temperature or below for six weeks.

Publications - USDA and Cooperative Program

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